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Heavy metals and pesticide residues as quality determinants for sustainable management of prawns along the Indian coastline of Tanzania

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**HEAVY METALS AND PESTICIDE RESIDUES AS QUALITY
DETERMINANTS FOR SUSTAINABLE MANAGEMENT OF PRAWNS
ALONG THE INDIAN COASTLINE OF TANZANIA**

Gloria F. Patiri

**A Dissertation Submitted in Partial Fulfillment of the Requirements for the Degree of
Master's in Life Sciences of the Nelson Mandela African Institution of Science and
Technology**

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ABSTRACT

The presence of heavy metals and pesticide residues in prawns, water and sediments, were determine. Prawns, sediments and water samples were collected along prawns fishing zones in the Indian coastline of Tanzania. Zinc (Zn), lead (Pb) and cadmium (Cd) were analyzed using Atomic Absorption Spectrophotometry (AAS). Direct Mercury Analyzer (DMA) was used for mercury (Hg) analysis. Pesticide residues were analyzed by Gas Chromatography-Mass Spectrophotometry (GC-MS). Information on stakeholder's perception on the sources of aquatic pollution was collected using a structured questionnaire. Results indicated that, fertilizer (60.7%), pesticides (59.8%) and herbicides (60.7%) were the main sources of aquatic pollution. *Cyberdip* and *Utupa*-mixed local herbs were the chemicals used in prawns fishing. Heavy metal contaminants were predominant in sediments followed by prawns, and water. The heavy metals were highly concentrated in prawns and sediments in the order of $Zn > Pb > Cd > Hg$, and $Pb > Zn > Cd > Hg$ in water respectively. *Lambda*-cyhalothrin was the only pesticide residue detected in prawns and sediments but not in water. *Lambda*-cyhalothrin levels detected in prawns from Kisiju and Kilwa were 5.6 – 45.2 folds above the maximum acceptable limits. *Lambda*-cyhalothrin levels in sediments was 175; 4070 and 4432 folds higher than the maximum acceptable level in Bagamoyo, Kilwa and Kisiju respectively. Presence of Zn, Pb and *lambda*-cyhalothrin beyond acceptable limits in prawns and sediments may indicate marine pollution. The maximum acceptable level of *lambda*-cyhalothrin in sediments is 0.00372 mg/kg and the maximum acceptable level of *lambda*-cyhalothrin for prawns is 0.05 mg/kg. These pollutants may impair quality and safety of prawns and by-products which is a risk to the public health. Therefore, monitoring of agricultural and the anthropogenic activities around prawn fishing areas is inevitable.

DECLARATION

I, **Gloria F. Patiri** do here declare to the Senate of Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and it has not been submitted for degree award in any other institution.

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CERTIFICATION

The undersigned certify that, they have read the dissertation titled “Heavy Metals and Pesticide Residues as Quality Determinant for Sustainable Management of Prawns along the Indian Coastline of Tanzania” and recommend for examination in fulfillment for the requirements for the degree of Master’s in Life Sciences of the Nelson Mandela African Institution of Science and Technology.

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DEDICATION

This work is dedicated to my beloved husband Felix W. Lyatuu, my children (John and Frankline) and my parents Mr. and Mrs. Felix Patiri for their love, support, encouragement and motivation in my academic journey.

TABLE OF CONTENTS

ABSTRACT	i
DECLARATION	ii
COPYRIGHT	iii
CERTIFICATION	iv
ACKNOWLEDGEMENT.....	v
DEDICATION.....	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF APPENDICES	xii
LIST OF ABBREVIATIONS AND SYMBOLS	xiii
CHAPTER ONE	1
INTRODUCTION	1
1.1 Background of the problem.....	1
1.2 Statement of the problem	2
1.3 Rationale of the study	3
1.4 Objectives.....	3
1.4.1 General objective	3
1.4.2 Specific objectives	3
1.5 Research questions.....	4
1.6 Significance of the study	4
1.7 Delineation of the study	4
CHAPTER TWO	5
LITERATURE REVIEW	5
2.1 Fish Production.....	5
2.2 Life cycle of prawns.....	5

2.3	Distribution of prawns	7
2.4	Prawns production	8
2.5	Development of prawn fishery in Tanzania	8
2.6	Management Measures of Prawns	9
2.6.1	Registration Fees and Fishing license	9
2.6.2	Vessel Observers	9
2.6.3	Establishment of Fishing Zones and Rotational Fishing	10
2.6.4	Fishing Time.....	10
2.6.5	Fishing Seasons	10
2.6.6	Vessels Capacity	11
2.7	Aquatic Pollutants.....	11
2.7.1	Heavy Metals.....	14
2.8	Pollution in Tanzania	23
CHAPTER THREE.....		26
MATERIAL AND METHODS.....		26
3.1	Material	26
3.1.1	Chemicals and reagents.....	26
3.1.2	Sample collection.....	27
3.2	Decontamination procedures	27
3.3	Methods.....	28
3.3.1	Study area	28
3.3.2	Study design	29
3.3.3	Sample size	30
3.3.4	Data collection tools	30
3.3.5	Collection of samples.....	30
3.3.6	Sample preparation for heavy metal (Pb, Cd and Zn)	31
3.3.7	Sample digestion for heavy metal (Pb, Cd and Zn).....	32

3.3.8	Heavy metal quantification	33
3.3.9	Mercury quantification.....	34
3.3.10	Pesticide residues analysis	35
3.4	Data analysis.....	37
CHAPTER FOUR.....		38
RESULTS AND DISCUSSION		38
4.1	Demographic characterization.....	38
4.2	Stakeholder perception on sources of aquatic pollution	40
4.3	Pesticide residues.....	42
4.4	Heavy Metals.....	44
CHAPTER FIVE		47
CONCLUSION AND RECOMMENDATION		47
5.1	Conclusion.....	47
5.2	Recommendations.....	47
REFERENCE		48
APPENDICES		65
RESEARCH OUTPUTS		88

LIST OF TABLES

Table 1:	List of prawn species found in Tanzanian marine waters.....	7
Table 2:	Prawn production data in Tanzania from 1993 to 2016.....	8
Table 3:	Types of pesticides and their mechanism	19
Table 4:	Study on pesticide residues done in Tanzania.....	23
Table 5:	Chemicals and reagents.....	26
Table 6:	Laboratory equipment.....	27
Table 7:	Demographic characteristics of respondents in the prawns fishing zone	38
Table 8:	Socioeconomic activities around the fishing zones	39
Table 9:	Agricultural inputs used in the study area.....	41
Table 10:	Chemicals used in illegal fishing in the study areas	42
Table 11:	Presence of active ingredient in the pesticides/herbicides from the fishing zones	42
Table 12:	<i>Lambda</i> -cyhalothrin concentration in sediments in the fishing zones.....	43
Table 13:	<i>Lambda</i> -cyhalothrine concentration in prawns in the fishing zone.....	44
Table 14:	Lambda-cyhalothrin levels in water in fishing zones	44
Table 15:	heavy metals concentration in the study zones:	46

LIST OF FIGURES

Figure 1: Life cycle of prawns (Montgomery, 2010)	6
Figure 2: A map of Tanzania showing sampling points in the prawns fishing zones along the Indian coastline of Tanzania Bagamoyo, Kisiju and Kilwa zones.	29

LIST OF APPENDICES

Appendix 1:	Questionnaire.....	65
Appendix 2:	Statistical analysis for questionnaires data.....	69
Appendix 3:	Statistical results for pesticide residue <i>Lambda</i> -cyhalothrin.....	76
Appendix 4:	Standard calibration curve.....	78
Appendix 5:	R-codes for heavy metals	81
Appendix 6:	Mean separation in heavy metals.....	86

LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variance
Cd	Cadmium
CPU	Catch Per Unit Effort
CAC	Codex Alimentarius Commission
EAMFRO	East African Marine Fisheries Research Organization
FAO	Food and Agriculture Organization of the United Nations
g	Gram
>	Greater than
Hg	Mercury
Hp	Hose Power
kg	kilogram
<	Less than
µg	Microgram
MLF	Ministry of Livestock and Fisheries
min	Minutes
MNRT	Ministry of Natural Resources and Tourism
MOP	Mwananchi Ocean Product
nm	Nanometer
NPK	Nitrogen Phosphorous Potassium
Pb	Lead
%	Percentage
PFMP	Prawn Fishery Management Plan
SWIOFC	South West Indian Ocean Fisheries Commission
TAFICO	Tanzania Fishing Cooperation
TAFIRI	Tanzania Fisheries Research Institution
Zn	Zinc

CHAPTER ONE

INTRODUCTION

1.1 Background of the problem

Prawns are short lived invertebrates that feed in sediments and their life cycle is from 12 to 18 months (Silas, 2011). The species inhabit beaches and shelter in mangroves and estuaries, to complete their life cycle, prawns have to go through two major ecosystems which are the off shore and the coastal inshore. Mature prawns usually breed in deep water while post larval and juvenile stages inhabit estuaries, blackish water and mangrove forest. Then, they migrate back to the sea to mature and breed (Silas, 2011). This species is among the most economically important in the world, where over 60% of it is traded internationally. However, the total global production of wild caught prawns has shown to increase from 3.3 million metric tons in 2010 to 3.8 million metric tons in 2014 (Valderrama & Anderson, 2011). Prawns are the most valuable marine species in term of income and export value in Tanzania and worldwide, also it contributing to socio-economic welfare of the coastal communities (PMP, 2012). Furthermore, the species are harvested in many countries including China, Thailand, Vietnam, Indonesia, America, Australia, Madagascar and Tanzania.

In Tanzania, prawns fishing is mostly done around the Rufiji Delta, about 200 km South of Dar-es-Salaam, and in some areas within Bagamoyo (Haule, 2001). But about 80% of prawns are found in the mangrove forest, which is the feeding and nursery ground for many fish species including prawns, crabs and shellfish (Daffa, Bayer, Mahika & Tobey, 2003). For that behavior, prawns fisheries have been categorized into artisanal fishery and commercial fishery in this country (Abdallah & Arnason, 2004). Commercial fishery operated off shore using advanced gear including trawling whereas artisanal fishery operates close to the shore (inshore fishers) using simple locally made fishing gears such as boat-seines, drift-net, set gill-net, cast-net, traps and beach-seining (Abdallah & Arnason, 2004). There are six dominant species of prawns harvested in Tanzania namely, white prawns (*Penaeus indicus*) that leads in terms of catch, giant black prawns (*Penaeus monodon*), tiger prawns (*Penaeus semisulcatus*), brown prawns (*Metapenaeus monoceros*), *Penaeus japonicas* and *Penaeus latisulcatus*.

The government of Tanzania through the Ministry of Livestock and Fisheries has reported decline of prawns production from the year of 2004 (PMP, 2012). The decline was anticipated to be due to high fishing effort from commercial prawn trawlers, which were introduced in 1987. Therefore, the Fisheries Department decided to impose a moratorium in 2007 to protect against further decline and allow stocks to recover. Even after imposition of moratorium the exploitation of this resource continued from artisanal fishing that even used illegal methods including chemicals (Katikiro, 2014), poor rice cultivation and vegetable agricultural practices that released pesticides to the prawns farms and mangroves hence pollution around the area (Francis & Mmochi, 2003). Due to rice cultivations negative in this area the effects have been reported due to the use of pesticides as many rice farms are very close to the water bodies (Stadlinger, Mmochi, Dobo, Gyllbäck & Kumblad, 2011).

Chemicals pollutants in seafood's apart from agricultural practice can also be produced from destructive fishing methods including use of chemicals that destroy important habitats for fish (Jiddawi & Öhman, 2002). As seafoods are highly perishable so to maximize its quality and value, freshness quality must be maintained throughout the supply chain from harvesting to consumers (Ryder, Iddya & Ababouch, 2014). Additionally, discharged untreated industrial wastes may contain toxic metal like Hg, Pb, Cd and Cr, which enter the coastal areas through rivers and streams and eventually to the sea foods (Rumisha *et al.*, 2017). These pollutants get stored in sediments making them to be the indicator of presence of heavy metal in the aquatic environmental (Mohammed, 2002). Once more, the pollutants including heavy metals and pesticide residues are among the causes for the decline of prawns production as they accumulate in the tissues and impair their biological functions (Rumisha, Mdegela, Kochzius, Leermakers & Elskens, 2016). Therefore, assessment of the presence of heavy metals and pesticide residues and their levels of toxicity in prawns and the environment is important for controlling and monitoring their sources hence the aim of this study.

1.2 Statement of the problem

The sustainability of prawns fishing in Tanzania has been questionable for years. Most of studies in fisheries have concentrated in stock assessment, reproduction cycles, depletion of prawns and fishing practices and the management measures of the resource have been based on findings from such studies. For instance, the introduction of prawns fishing moratorium in 2007 was based on the reports of depletion of prawns in all fishing grounds. To reduce the fishing pressure on prawn, the moratorium suspended all commercial fishing licenses and

allowed only artisanal fishing. Additionally, the government has also consolidated the licensing of artisanal fishing to avoid overfishing, enhance monitoring of prawns fishery habitats, ensure local utilization of prawns through strengthening prawns data collection, analysis, management and dissemination of findings to stakeholders (PMP, 2012).

Despite the effort of government to sustain the prawns fishing industry in Tanzania, the quality of prawns products in Bagamoyo and Kibiti districts have been rarely researched. Recent studies (Rumisha *et al.*, 2017; Rumisha *et al.*, 2016) have reported presence of high level traces of copper (Cu), iron (Fe) and Zn in giant tiger prawn (*Penaeus monodon*) in Rufiji, Pangani and Wami estuaries. Therefore, this study aimed to expand the knowledge on the quality of prawns by quantifying the levels of heavy metals and pesticide residues so as to advocate the mitigation measures to sustain the industry. This study was carried out in Bagamoyo district covering the villages of Dunda, Kisutu and Magomeni. Also in Kibiti district within Kisiju zone (Nyamisati and Kikale) and Kilwa zone (Mbwera and Ruma) known for prawns production and fishing along the Indian coastline of Tanzania.

1.3 Rationale of the study

The rationale of the study was to know the stakeholder perception on sources of heavy metals and pesticide residues and to determine levels of pesticide and heavy metals Zn, Pb, Cd and Hg along the Indian coastline of Tanzania specifically in the study zones of Bagamoyo, Kilwa and Kisiju. The study provides the levels of heavy metals and pesticide residues which might be useful in quality management of prawns' safety. Again the study may contribute to the establishment of guidelines to manage and monitor prawns fishing areas including measures to fight against illegal prawns fishing.

1.4 Objectives

1.4.1 General objective

To assess presence of pollutants in prawns, water and sediments in selected villages of in Bagamoyo, Kilwa and Kisiju zones.

1.4.2 Specific objectives

- (i) Assessing stakeholder's perception on sources of pollution in the selected prawns fishing zones.

- (ii) To determine the levels of heavy metals (Hg, Pb, Cd and Zn) and pesticide residues in prawns, sediments and water in the prawns fishing zones.

1.5 Research questions

- (i) What are stakeholder's perception on sources of aquatic pollution in the selected prawns fishing zones?
- (ii) What are the levels of heavy metals (Hg, Pb, Cd and Zn) and pesticide residues in prawns, sediments and water in the prawns fishing zones?

1.6 Significance of the study

The study provides information and understanding on the stakeholder's perception on sources of pollution and levels of contaminants in marine environment and products (prawns) so as to safeguard the health of consumers and marine biodiversity. Additionally the information on the presence of chemical pollutants, is important as a quality and safety indicator of prawns' quality, consumed as a very good source of protein and minerals. Furthermore, the study provides insightful information on chemicals used in illegal fishing activities and dynamite fishing. Again it provides the levels of heavy metals and pesticide residues which might be useful in quality management of prawns' safety. And as well may contribute to the establishment of guidelines to manage and monitor prawns fishing areas including measures to fight against illegal prawns fishing.

1.7 Delineation of the study

The study was done along the Indian coastline of Tanzania, in Kibiti and Bagamoyo districts specifically on the prawns fishing zones of Bagamoyo Kilwa and Kisiju and the sampling points was taken by GPS.

CHAPTER TWO

LITERATURE REVIEW

2.1 Fish Production

Recently, the annual growth rate of fish per capita has exceeded that of meat suggesting that fisheries and aquaculture are important sources of protein and food security at large (FAO, 2018). The growth rate of fish per capita has grown from 67% in the 1960s to about 88% in 2017, and twice as high as population growth worldwide. In Tanzania, fisheries sector plays an important role in food security and economic development (AFSR, 2016). The fish per capita in Tanzania has been estimated to about 7.7 kg. Fish and fishery products are important source of protein and essential micronutrients to poor communities providing about 3 billion people with about 20% of their protein intake. The sector contributes about 1.4% of the national Gross Domestic Product (GDP). A total of 183 223 people, mostly fishers, directly depend on various fisheries resources to derive their livelihood (AFSR, 2016). For instance, in 2016, the fish production was 362 594.89 metric tons that valued 1.4 billion Tanzania Shillings. The country earned 14.3 billion as foreign exchange from export of 39 691 462.0 metric tons of fish and fish products in the same year and import of fish and fisheries products from the foreign countries was 13 917 656.98 kilograms and royalties earned from imports was 8.5 billion Tanzania shillings (AFSR, 2016). Prawns are among the valuable fishery products with an estimated average value of USD 3800 per ton in 2016 worldwide (FAO, 2018).

2.2 Life cycle of prawns

The life cycle of prawns begins with planktonic larvae with a variety of nauplius, protozoa and post-larval stages, followed by juvenile and adult stages (Fig. 1). Prawns usually spawn offshore, then the larvae migrate to the inshore nursery areas for shelter and food in dry season using a combination of tidal currents and diurnal vertical migration patterns (Montgomery, 2010). They spend three to four months and grow to juvenile stages (Silas, 2011), while the adults migrate back to the open sea for spawning (Montgomery, 2010).

In Tanzania, prawns spawning is mainly seasonal (Bwathondi *et al.*, 2002) and migrate to the open sea during the rainy season, usually from October to December (Silas, 2011). The spawning peak of prawns occurs in January to March and the new recruited ones appear in the coastal waters from February to May (Teikwa & Mgaya, 2003). Large population of

juvenile prawns are recruited to the fishable of lower salinity areas in estuaries (Teikwa & Mgaya, 2003). Pre-adults and adults are usually found in large numbers along the coast during the heavy rain season between March and May (Teikwa & Mgaya, 2003).

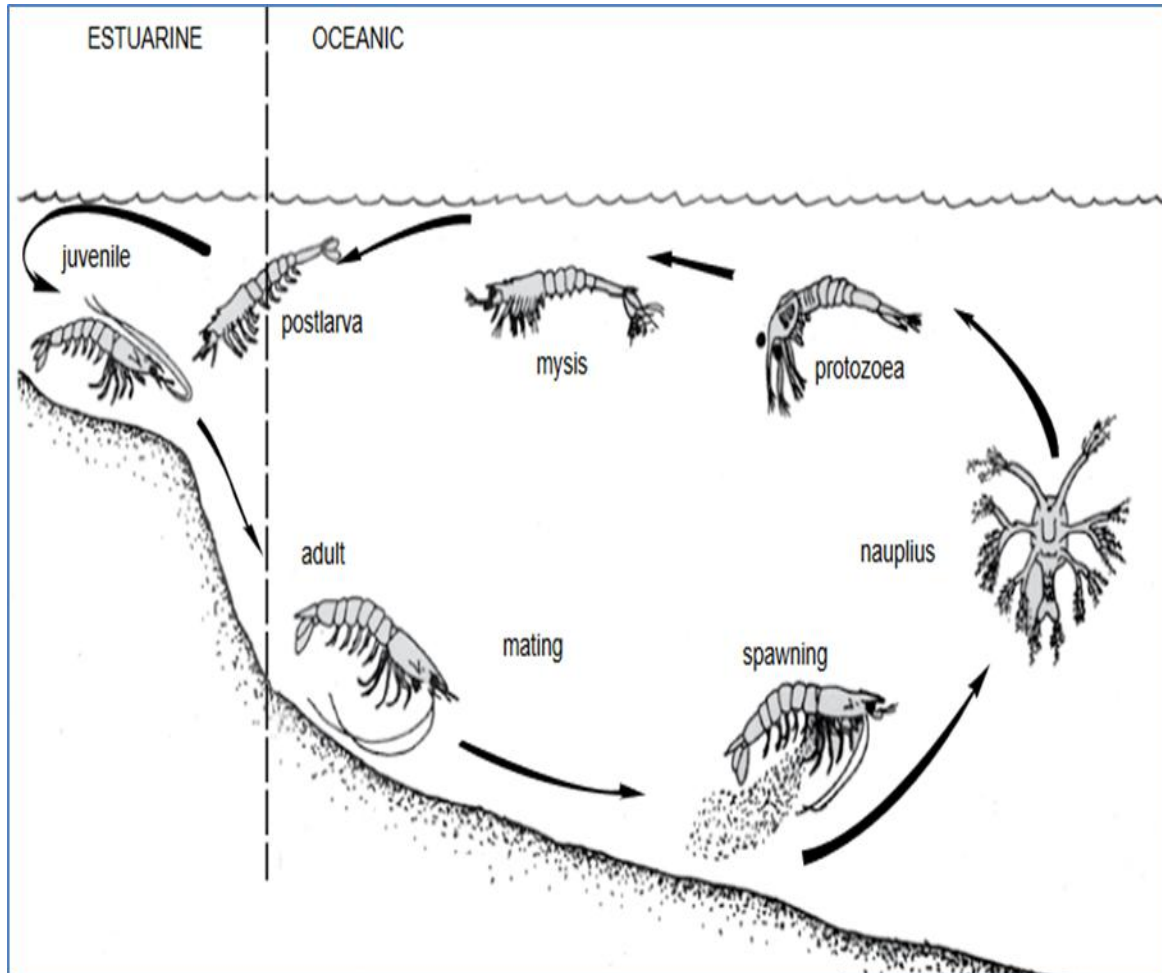


Figure 1: Life cycle of prawns (Montgomery, 2010)

However, the Indian Ocean has high biodiversity hotspot of marine fauna and flora species including corals, mangroves, sea grasses, fishes, marine mammals, turtles, crustaceans and mollusks (Keesing & Irvine, 2005). In this ocean prawns have been harvested for a long time using tradition fishing techniques, marketed and consumed locally, as well as for export (Silas, 2011). Again, harvesting of fish has been a major source of daily income and food for people living along the coastline of Tanzania. The Wami, Ruvu and Pangani river estuaries also provide wide range of diversity of fish to Bagamoyo residents. Likewise, Kilwa and Kisiju zones are fed by Rufiji delta within the coastline of the Indian Ocean of Tanzania (Shaghude, 2004). In the Rufiji delta, various agricultural activities are simultaneous carried out with prawns farming. As matter of fact pesticide residues from the rice farms in

mangrove areas have been reported to affect the performance of prawns and jeopardize the health of people eating prawns (Shagude, 2004).

2.3 Distribution of prawns

There are about 318 prawns' species in the world (Silas, 2011). In Tanzania, only eleven species have been identified in marine waters (Table 1). However, there are only six species that are dominant and of economic value in Tanzania (Bwathondi *et al.*, 2002). Out of the six species, *Penaeus indicus* has been the most dominant in Tanzania constituting about 60% of the total prawn catches (Teikwa & Mgaya, 2003). Other species are found in all coastal zone regions including Tanga, Mtwara, Lindi, Coast and Dar es Salaam. Moreover, the majority of the catches are found in Kibiti and Bagamoyo districts in the Coast region. The high prawn's fishing area is categorized into three zones, namely Bagamoyo, Kilwa and Kisiju (Bwathondi *et al.*, 2002). Bagamoyo is the least productive area contributing about 25% of the total annual prawn catches in the country (Silas, 2011). The dominant prawn species in the zones are *Penaeus indicus* and *Metapenaeus monoceros*. Kisiju zone is the most productive prawn fishing zone contributing about 45% of the total annual prawn catches. The dominant prawn species in this zone are *Metapenaeus monoceros* and *Penaeus indicus*. On the other hand, Kilwa zone is the second most productive area contributing about 30% of the total annual prawn catches whose dominant species are *Metapenaeus monoceros*, *Penaeus semisulcatus* and *Penaeus indicus*. Prawns are the most important source of income and protein to the human populations in the Coast region of Tanzania.

Table 1: List of prawn species found in Tanzanian marine waters

No.	Scientific name	Common name
1	<i>Penaeus indicus (Fenneropenaeus) indicus</i>	White prawn
2	<i>Metapenaeus monoceros</i>	Brown prawn
3	<i>Penaeus semisulcatus</i>	Tiger prawn
4	<i>Penaeus monodon</i>	Giant prawn
5	<i>Penaeus (Marsupenaeus) japonicus</i>	Flower prawn
6	<i>Exhippolysmata ensirostris</i>	Hunter shrimp
7	<i>Macrobranchium rude</i>	Hairy river prawn
8	<i>Nematopalaemon tenuipes</i>	Spider prawn
9	<i>Metapenaeus stebbingi</i>	Peregrine Shrimp
10	<i>Penaeus (Melicertus) canaliculatus</i>	Witch prawn
11	<i>Penaeus (Melicertus) latisulcatus</i>	Western king prawn

Sources: Mwakosya (2004)

2.4 Prawns production

In Tanzania, prawns production continued to drop year after year. According to the fisheries annual report (1993 – 2016), the amount of prawns has been decreasing from the year 2004 to 2016 as indicated in Table 2.

Table 2: Prawn production data in Tanzania from 1993 to 2016

Year	Prawns catch m ³ tons	Year	Prawns catch m ³ tons
1993	1462	2004	661
1994	2513	2005	467
1995	2108	2006	312
1996	1779	2007	202
1997	2091	2010	2
1998	2778	2011	17
1999	2252	2012	125
2000	99	2013	104
2001	497	2014	17
2002	2521	2015	1
2003	3664	2016	1

Source: Annual Statistics, Department of Fisheries (MLF, 2016)

2.5 Development of prawn fishery in Tanzania

The first study on taxonomy of prawn was conducted by the East African Marine Fisheries Research Organization (EAMFRO) using trawl survey in 1959 (Bourjea *et al.*, 2008). Mwananchi Ocean Product (MOP), a Japanese firm entered into prawn fishery during 1960s and collapsed in early 1970s (Silas, 2011). In 1974, the Government of Tanzania established Tanzania Fishing Cooperation (TAFICO), a parastatal organization to promote the prawn fishing industry, which was based on two species, namely *Penaeus indicus* and *P. monodon*. The company was closed in 1999 due to poor administration that resulted into operating under loss (Haule, 2001). Commercial prawn fishery became more intensive after implementation of liberalization policy in 1987 when Kenya and Greece fishing vessels were licensed fishery for prawns until 2003 when the maximum number reached was 26 (Abdallah & Arnason, 2004). During that period, most of the foreign trawlers registered in Tanzania exported their products to Europe.

Furthermore, industrial fisheries statistics indicated that the catch per unit effort (CPUE) of prawns had decreased from 610 kg per day in 1990 to 271 kg per day in 2000 caused by either high number of fishing vessels or increased fishing capacity of the fishing vessels (Abdallah & Arnason, 2004). Additionally, the number of fishing days has been reported to

increase (Silas, 2011). On the other hand, catch rates have decreased from 63 kg/h to 5 kg/h (Bwathondi *et al.*, 2002). Moreover, the prawn stocks in Tanzania have been highly exploited to the extent of collapsing (Haule, 2001).

The decline of prawn fishery is hypothesized to be due to increase in industrial fishing pressure (Bwathondi *et al.*, 2002). Prawn stock along the Tanzanian coast decreased from about 2000 metric tons in 1970s to 1000 metric tons in early 1980s (Silas, 2011). The Ministry of Natural Resources and Tourism, in collaboration with the South West Indian Ocean Project estimated a maximum sustainable yield (MSY) of 1050 metric tons during 1990s. The stock has continued to decrease up to 497 metric tons in 2001 (PMP, 2012). These findings suggest that the stock has declined to more than 50% over the past two decades.

2.6 Management Measures of Prawns

Management measures and policies have been formulated and enforced by the Fisheries Division from early 1987 to ensure sustainable harvest of prawns in the country (Haule, 2001). The management measures introduced to control the level of effort included registration fee and fishing licenses, restrictions on fishing power, vessel licenses, fishing time, gross registered tonnage, closed season and vessel observers (Silas, 2011).

2.6.1 Registration Fees and Fishing license

This regulation was approved in 1987 and all vessels were required to be registered for the first time by the Fisheries Division in Tanzania. Registration fees were based on gross registered tonnage, shore infrastructure and processing facility (Wilson, 2004). For example, vessels registered in Tanzania with land processing facility were charged 5 712 Tshs for fishing and fishing vessel license whereas vessels without land processing facility were charged 257 040 Tshs for fishing and 385 560 Tshs for fishing vessel license (Wilson, 2004). Fishing license was paid annually and it was meant to track the number of active vessels that were involved in fishing, and these registration fees and fishing licenses were ways of collecting Government revenue (Wilson, 2004).

2.6.2 Vessel Observers

This measure was introduced in 1987 with the aim of resolving the conflicts between commercial and artisanal fishers who were concerning with industrial fishing activities near

shore, and to ensure that all regulations were followed. Observers from the Fisheries Division were supposed to be onboard in each of the fishing vessel licensed to the fishery, but due to lack of financial support, the Fisheries Division decided to deploy only one or two observers to monitor all fishing activities of all vessels in the fishing area (Haule, 2001).

2.6.3 Establishment of Fishing Zones and Rotational Fishing

This regulation was introduced in 1988, the Government through Fisheries Division introduced rotational trawling to ensure that effort is not concentrated in one fishing Zone (Haule, 2001). Before this regulation, most of the Kenyan fishing vessels was concentrated in Zone 2 (Kisiju and Rufiji). The rotational system was also intended to encourage fishing vessels to search for new grounds and minimize conflicts among trawl operating companies and between these companies and artisanal fishermen (Mongi, 1990). However, the problems still existed between industrial and artisanal fishermen. To resolve this problem, regulation of fishing time was introduced.

2.6.4 Fishing Time

Fishing time regulation measure was established to resolve the conflict between Industrial and artisanal fishermen. It was introduced in 1990 to restrict industrial trawlers from fishing at night and allowing artisanal fishers set their nets at night and haul at dawn (Haule, 2001). During day time (06:00 AM to 06:00 PM) artisanal and industrial fishers were both fishing together because captain could see set nets. This regulation reduced fishing time for industrial fisherman from 24 hours in a day to 12 hours (Haule, 2001).

2.6.5 Fishing Seasons

This regulation was introduced in 1990 to protect immature shrimps. The season was being opened for seven months from March to September for Industrial fishers. This was necessary because data collected by TAFIRI showed higher prawn juveniles in catches from November to March. In 1992, after TAFIRI has carried out another trawl survey, it was further recommended to extend the closed season from four to five months starting 1st December to 30th April each year after evident declining catches in the survey (Bwathondi *et al.*, 2002). But, this management measure was never implemented due to lack of financial support for monitoring, control and surveillance.

2.6.6 Vessels Capacity

Vessels capacity regulation was introduced in 1997 to restrict vessels with engine capacity of more than 500 Hp from fishing (Haule, 2001). This was established with the purpose of controlling fishing capacity by making sure the vessel used are small hence do not allowed to fish too much. This was successful because only vessels with less than 500 Hp were allowed to fish from 1997 (Wilson, 2004).

2.7 Aquatic Pollutants

Environmental pollution such as heavy metals and pesticide residues have been a major concern worldwide (Abd-El, 2012). Marine environment can be polluted by many substances, consequently increased health risks to marine inhabitants such as fish and shellfish and other organisms that feed on them including human beings (Walker & Livingstone, 2013). Pollutants from sea water, suspended particles, sediments and food chains can cause bioaccumulation (Walker & Livingstone, 2013). Availability of aquatic pollution is directly proportional to the rate at which accumulation occurs in an organism depends on the availability of the pollutants, and on biological, chemical and environmental factors (Apraiz *et al.*, 2006). However, heavy metals and pesticide residues as among the pollutants are of global concern as they pose adversely affects to the ecosystem and human health (Marković *et al.*, 2010). Deposited heavy metals and pesticide residues in a river system through different methods including rains undergo changes due to dissolution, precipitation and sorption which affect their performance and bioavailability (Alloway & Ayres, 1997). Furthermore, presence of heavy metals and pesticide residues in prawns, water and sediments indicates waste discharges on the riverine ecosystems from agricultural, anthropogenic and industrial sources (Bayen, 2012). Recently, heavy metals and pesticide residues pollution is the main problem in many developing countries (Odada *et al.*, 2004) Tanzania inclusive.

According to Sarkar *et al.* (2016), heavy metals and pesticide residues are potentially gathered in aquatic environments including prawns, water, and sediments. A study by Machiwa (1992) has reported accumulation of pesticides such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), and heavy metals, in the coastal sediments. Heavy metals and pesticide residues in aquatic environment have been reported worldwide (Machiwa, 1992; Saha *et al.*, 2016; Sarkar *et al.*, 2016; Sobihah *et al.*, 2018; Wandiga *et al.*, 2002). Furthermore, heavy metals and pesticides contamination can be dangerous to public health as they can compromise with safety and quality of the prawns

(Pigott, 2017). Rumisha *et al.* (2016) is the only recent report on heavy metals contamination in prawns in Dar-es-Salaam, Tanzania. Besides, no studies have focused on heavy metals and pesticide residues in Bagamoyo, Kisiju and Kilwa zones, specifically in Kikale, Nyamisati, Ruma, Mbwera, Kisutu, Dunda and Magomeni villages. In other words, to date, there is no scientific information on heavy metal pollution and pesticide residues in prawns, water and sediments in the mentioned areas.

Nonetheless fishing, aquaculture, tourism and recreation are activities that constitute the main sources of livelihood and income to the local communities as a results of estuaries that allow diversity of plant and animal life (Elliott & Whitfield, 2011). The estuaries are also a place for fine grain sediments and contaminants, and as well serve as secondary sources of organic and inorganic pollutants in marine environments (Elliott & Whitfield, 2011; Ranjan *et al.*, 2012). Anthropogenic changes in estuaries play an important role in climate like precipitation and flooding events. These changes influence the distribution of various organic and inorganic pollutants that impact the flora and fauna in these sensitive and dynamic ecosystems (Shilla & Routh, 2018). The fact that, untreated wastes loaded with heavy metals, pesticide residues and other pollutants produced from various development sectors go directly to aquatic environments (Shilla & Dativa, 2011) and pollute it. These pollutants persist in the aquatic environments and bioaccumulate in various environments. Nevertheless, pollutants present in the environment in small concentrations become part of various food chains through bio-magnification and their concentration which increases to levels that are toxic to organisms higher in trophic levels, including humans (Burger *et al.*, 2002).

The organic pollutants like polycyclic aromatic hydrocarbons (PAHs) are persistent and ubiquitously distributed in the environment and can be easily traced in air, water, soil, sediments, plants, animals, and human beings, their presence in the aquatic environment is closely related to anthropogenic sources (Soclo, Budzinski, Garrigues & Matsuzawa, 2008). The distribution of polycyclic aromatic hydrocarbons in aquatic ecosystems are influenced by various factors which are salinity, pH, suspended particulate matter load, tidal currents and seasonal variability (Shilla & Routh, 2018). Environmental distribution of polycyclic aromatic hydrocarbon is always associated with anthropogenic activities such as fossil fuel combustion, waste incineration, coal gasification, liquefaction processes, petroleum cracking, and production of coke, black carbon, coal tar, pitch and asphalt (Yunker *et al.*, 2002). As a results from those compounds wastewater, sewage, runoff from roads, street dust, oil spills

and vehicular/maritime traffic are released into the aquatic environment through industrial activities (Ranjan, Routh, Ramanathan & Klump, 2012).

Similarly, these polycyclic aromatic hydrocarbon are very hazardous compounds, as the compound are carcinogenic and mutagenic to both terrestrial and aquatic organisms (Yunker *et al.*, 2002). For that case, it is important to know the processes which govern the behavior of these contaminants in aquatic systems to establish their potential toxic effects on water and biota. This dynamic ecosystem is very sensitive to the regional climate, flooding events, hydrological changes, and human interactions in both the upstream and downstream riparian areas of the Rufiji river system. Previous studies on the Rufiji ecosystem indicated high concentrations of pesticides, metals and combustion related contaminants (Gaspere, Machiwa, Mdachi, Streck & Brack, 2009). Although at present the Rufiji estuary and its delta can be considered as one of the less polluted coastal areas in Tanzania, the presence of small scale industries, agricultural activities, commercial fishing and other socioeconomic functions associated with fossil fuel combustion and its discharge suggest that polycyclic aromatic hydrocarbon (PAHs) might also be released in significant amounts to this coastal environment as pollutants.

Differential sensitivity to pollution of fish has cause to be widely documented as useful indicators of quality of water. Pollutants enter in water bodies from a variety of sources, such as soil and rocks that are directly exposed to surface waters, and fallout of atmospheric particulate matter (Walker & Livingstone, 2013). Additionally, a large amount of domestic and industrial wastes are always released to the aquatic environment without any prior treatment, as the metals are derived from the industrial areas through rivers and storm water outflows (Shilla, 2016). Likewise, estuarine areas are of considerable important ecological, environmental, and economic value to the coastal and inland communities (Shilla & Routh, 2018).

Nevertheless trace metal input like pesticides, industrial sewage, burning of fossil fuels, mining, and smelting are human activities in which when expose can results to trace metal pollution around the mangroves located in intertidal areas of the coastal region (Anouti, 2014). Trace metal have high capacity for binding ability for that behavior cause the mangrove forest to tolerate high levels of trace metal as it rich with sulfide content that can absorb various metals and increase their concentrations in mangrove sediments (MacFarlane,

Koller & Blomberg, 2007). Also availability of these metals result to bioaccumulation in various plant tissues (Lotfinasabasl & Gunale, 2012).

Besides, biodiversity in marine ecosystems can be disturbed by trace metal pollution because of bioaccumulation ability in the marine food chain (Chakraborty, Zaman & Mitra, 2014). Factors which are responsible for accumulation of trace metals and affects its distribution in coastal areas, includes salinity, pH, hardness and temperature. Mangrove ecosystem in Rufiji delta is a dynamic environment of various socio-economic importance which cause biologically diverse flora and fauna sensitive to regional climate change, hydrology, and anthropogenic activities. Urban development and agricultural activities in the catchment have affect the mangrove ecosystem, and pollution in upstream sections of the Rufiji river (Erftemeijer & Hamerlynck, 2005). In East Africa mainland Tanzania 20% drainage is from Rufiji river and the largest river (Erftemeijer & Hamerlynck, 2005). This river has potential purpose of transporting different types of pollutants from its catchment into the Rufiji delta, which supports the largest mangrove ecosystem in East Africa (Richmond, Wilson, Mgaya & Le Vay, 2002). Livelihood of many riparian communities depends on fishery and other interdependent activities such as agriculture and pastoralism within the Rufiji delta. Hence investigation of marine pollutants is important as an indicator for sustainable management of prawns along the Indian coastline of Tanzania (Marchant & Hooghiemstra, 2004).

2.7.1 Heavy Metals

Heavy metal is a general collective term which applies to the group of metals and metalloids cadmium (Cd), zinc (Zn), mercury (Hg), copper (Cu), arsenic (As) and lead (Pb), which have high density and cannot be destroyed easily in organisms' bodies, thus very toxic even at low concentration (Duruibe *et al.*, 2007). Heavy metal cause bio-toxic effect with the general signs of gastrointestinal (GI) disorder when consumed above acceptable levels. Signs include diarrhea, stomatitis, tremor, hemoglobinuria causing rust red color to stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia and their effects can be neurotoxic, carcinogenic, mutagenic or teratogenicity (Duruibe, Ogwuegbu & Egwurugwu, 2007). In aquatic environment, copper (Cu) and zinc (Zn) are required in trace amounts for smooth function of different biological systems. However, accumulation of heavy metals in marine environments has become a problem throughout the world. These metals may accumulate to levels that can cause great effects on aquatic organisms (Giguère, Campbell, Hare, McDonald & Rasmussen, 2004).

There are two main routes of heavy metals exposure, the primary route, intake of these chemicals in aquatic organisms is via gills and the secondary route is through ingestion of food or sediment particles with subsequent transport across the gut (Jezierska & Witeska, 2006). Various studies outlined exposure through ingestion as the most important route of uptake (Schlekat, Decho & Chandler, 2000). Likewise heavy metals are known to distort the biological functions of biomolecules, and can interfere with metabolism, synthesis and transport of hormones (McCormick, O'Dea, Moeckel, Lerner & Björnsson, 2005). Their concentration in turn increases in the predators and finally in the human beings, resulting in the onset of various types of health problems (Fleming *et al.*, 2006). After a careful review of the existing literature it appears that not much attention has been paid towards studies on the distribution and environmental implications of heavy metals in water, sediment and prawns (Riddell, Culp & Baird, 2005). Lead however, has been shown to generate adverse effects in biological systems (Shilla, 2016). High concentration of Pb, Cr, Zn and Cu in sediments and tissues of biota has been reported especially in areas affected by anthropogenic activities (Shilla & Dativa, 2011).

Aquatic organisms including prawns get contaminated with heavy metals in aqueous from various anthropogenic activities that accumulate in their tissues causing chronic illness and potential damage to the population (Korkamaz, Ersoysal, Koroğlu & Erdem, 2019). The amount of contamination is high near specific source of emission related to industrial activities, disposal of waste, agricultural and animal husbandry practices. As trace metals are always very essential at low levels but usually very toxic at higher concentrations (Rainbow, 2007). Human get affected through food chain causing various diseases and damages (Pandey & Madhuri, 2014). But both natural and anthropogenic activities attributes to heavy metals and pesticide residues in the environment. Increasing pollution of heavy metals and pesticide residues chances of significant adverse health effects for invertebrates, fish, and humans also arises (Islam & Tanaka, 2004). Heavy metal pollution in aquatic ecosystems is increasing due to the effects from urbanization as well as industrialization toward pollution (Lin, Zhao & Marinova, 2009). Nevertheless, heavy metals pollution have been proven as health risks to more than 10 million people in various countries (Shakoor *et al.*, 2013). Fish is a potential indicator of presence of traces of heavy metals pollution (Bernet *et al.*, 1999).

Moreover bioaccumulation of metal toxins in the food chain results to disastrous effects on human health (Shakoor *et al.*, 2013). Some inorganic elements found in nature, such as

cadmium (Cd), mercury (Hg), lead (Pb) and arsenic (As), are considered potentially dangerous for human health if absorbed beyond certain limits (Shakoor *et al.*, 2013). For instance, in Linfen China, people faced extreme loads of pollution, in Haina of Dominican Republic people suffered from a huge amount of lead poisoning, and in Ranipet a city of India, about 3.5 million people were affected by tannery waste (Shakoor *et al.*, 2013). General signs of these heavy metals (Cd, Zn, Hg, copper (Cu), arsenic (Ar) and Pb) includes gastrointestinal (GI) disorder, diarrhea, stomatitis, tremor, hemoglobinuria causing rust red color to stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia and the effect could be neurotoxic, carcinogenic, mutagenic or teratogenicity (Duruibe *et al.*, 2007). Sediments have been widely used as environmental indicators to assess metal pollution in the natural water (Förstner & Wittmann, 2012). Below are some of the heavy metals which have the effect on aquatic organism.

(i) Cadmium

Cadmium is a toxic metal that accumulate naturally in marine organisms, but yet has no known metabolic role (Wang & Rainbow, 2007). It is relatively poorly absorbed into the body and like other metals, once absorbed get slowly excreted, Cd accumulates in the kidney causing renal damage (Fowler, 2009). Although lower levels are found in many foods, kidneys of animals are major sources of Cd and they are most consumed by human (Roesijadi, 1992). Fish contains only small quantities of Cd, while crustaceans and mollusks may accumulate larger amounts from the aquatic environment (Roesijadi, 1992). The principal toxic effect of Cd is its toxicity to the kidney, although it has also been associated with lung damage including induction of lung tumors and skeletal changes in occupationally exposed populations (Godt *et al.*, 2006). Tanzania lacks its own quality guideline for heavy metals (Mdegela *et al.*, 2009). According to Arulkumar (2017) the maximum acceptable levels of heavy metals for WHO/FAO 2015 in water supporting aquatic life is 0.008 mg/L, for sediments is 85 mg/kg (Duruibe *et al.*, 2007) and prawns is 2 mg/kg for Cd (Arulkumar, 2017).

(ii) Mercury

The main concern of Hg to human population, especially in young children is through food intakes (Bernhoft, 2012). Organic forms of Hg can cross the placental barrier between the mother and the unborn baby causing a range of neurological disturbances from impaired learning to obvious brain damage (Davidson, Myers & Weiss, 2004). Excessive exposure to

Hg is associated with a wide adverse health effects including damage to the central nervous system and kidney (Bernhoft, 2012). Mercury is very active in aquatic environment so people are exposed to it through the consumption of fish and prawns (Davidson *et al.*, 2004). Aquatic organisms such as fish including prawns and seaweeds get contaminated through disposal of waste water from industries, hospitals and water run-off from agricultural sites (Davidson *et al.*, 2004). The Hg_2^{2+} is a nontoxic while Hg^{2+} is fairly toxic this is because of high affinity for sulphur atoms of amino acids. The most toxic species are organomercurials, particularly CH_3Hg^+ . Methylation of mercury takes place in the activate environment as a result of activities of bacteria, fungi or enzyme (Dent, Forbes & Stuar, 2004). Usually, MeHg in sediments does not exceed 1.5% of the total Hg present so under various natural conditions inorganic mercury may be converted to very toxic methyl mercury (MeHg) compounds, which tend to bioaccumulate in the aquatic and terrestrial food chain (Horvat, Liang & Bloom, 1993). Evidence for the methylation mechanisms is still largely circumstantial that why in this study total mercury was determined and not MeHg. Tanzania lacks its own quality guideline for heavy metals Mdegela *et al.* (2009). According to Shao (2014), the WHO/FAO 2015 acceptable levels for Hg in water supporting aquatic life is 0.05 mg/L, sediments is < 1 mg/kg Duruibe *et al.* (2007) and prawns is 0.5 mg/kg (Arulkumar, 2017) were used as reference in this study.

(iii) Lead

Lead is a serious cumulative body poison, short-term exposure to high levels of Pb can cause brain damage, paralysis, anemia and gastrointestinal symptoms (Yedjou, Milner, Howard & Tchounwou, 2010). Longer-term exposure can cause damage to the kidneys, reproductive and immune systems in addition to effects on the nervous system (Yedjou *et al.*, 2010). Infants and young children are more vulnerable to the toxic effects of lead than adults. For instance, low level concentrations of Pb in the fetus through placental barrier interfere with intellectual development in young children (Gillis, Arbieva & Gavin, 2012). Consumption of food including fish contaminated with Pb is the major source of exposure for the general population (Gillis *et al.*, 2012). Since Tanzania lacks its own quality guideline for heavy metals (Mdegela *et al.*, 2009). According to Arulkumar (2017) the maximum acceptable levels of Pb in water supporting aquatic life is 0.0058 mg/L WHO/FAO 2015 sediments is 420 mg/kg (Duruibe *et al.*, 2007) and prawns is 0.3 mg/kg (Arulkumar, 2017).

(iv) Zinc

Zinc is an important trace element and plays a vital role in the physiological and metabolic processes of many organisms. At higher concentration, it can be toxic to organisms and plays an important role in protein synthesis (Shilla, 2016). Unlike many fish, prawns can accumulate and regulate Zn concentrations in their bodies up to 100 mg/kg even at exposure of high concentrations (Rahouma, Shuhaimi, Othman & Cob, 2013). Thus, at higher levels of dissolved Zn there is a sharp increase in body Zn concentration, but the body Zn concentration reaches a plateau. High Zn concentrations are mostly found in dead prawns (Rumisha *et al.*, 2016). Human being gets healthy effects through consumption of contaminated prawns and other edible aquatic organisms. Tanzania lacks its own quality guideline for heavy metals (Mdegela *et al.*, 2009). According to Arulkumar (2017) the maximum acceptable levels of Zn in water supporting aquatic life is 0.0766 mg/L WHO/FAO 2015, for sediments is 7500 mg/kg (Duruibe *et al.*, 2007) and prawns is 100 mg/kg (Arulkumar, 2017).

(v) Pesticides

Pesticides are chemicals used as insecticides, herbicides, fungicides, molluscicides, rodenticides, nematocides, and plant growth regulators to control weeds, pests and diseases in crops, and for the health care of humans and animals (Falis, Špalková & Legáth, 2014). Pesticides play an important role in modern agriculture by providing dependable, persistent and relatively complete control against harmful pests with less expense and effort hence enhanced crop productivity and drastic reduction of vector borne diseases (Damalas & Eleftherohorinos, 2011). Misuse of pesticides can affect flora and fauna (Oyugi, Chhabra, Njue & Kinyua, 2003), and pose potent pollutants to the environment with un-desirable adverse effects on non-target organisms such as fish (Alegria & Shaw, 1999).

Pesticides are as well can be classified according to their chemical properties, which are organophosphates, organochlorines (chlorinated hydrocarbons), carbamates and thiocarbamates, and pyrethroids (Table 3). These pesticides were intensively used over the years, as from that point of view there are concerns over the environmental quality of pesticides application as further described in Table 3.

Table 3: Types of pesticides and their mechanism

S/N	Chemical	Example	Characteristics	Mechanism of Action
1.	Organophosphates	<ul style="list-style-type: none"> - Chlorpyrifos - Dimethoate - Fenthion - Naled - Temephos - Trichlorfon 	<ul style="list-style-type: none"> - Made from phosphoric acid - Most are insecticides - They are highly toxic - It breaks down faster in the soil, food and feed 	These control pest by acting on the nervous system, interfering with the nerve impulse transmission, disrupting the enzyme cholinesterase that regulates acetylcholine (a neurotransmitter)
2.	Organochlorines (chlorinated hydrocarbons)	<ul style="list-style-type: none"> - Aldrin - Chlordan - Dieldrin - Endosulfa - Endrin 	<ul style="list-style-type: none"> - Generally persistent in the soil, food and in human and animal bodies. - They can accumulate in fatty tissues - Traditionally used for insect control and mites. - They do not break down easily. - Some such as DDT and Chlordane are no longer in use because they stay in the environment for a long time 	They control pests by disrupting nerve impulse transmission
3	Carbamates and Thiocarbamates	<p>Insecticides</p> <ul style="list-style-type: none"> - Carbaryl (banned due to health risks) - Propoxur - Methomyl - Carbofuran - Thiodicarb <p>Herbicides</p> <ul style="list-style-type: none"> - Barban - EPTC - Protham - Triallate <p>Fungicides</p> <ul style="list-style-type: none"> - Nabam 	<p>They are made from carbamide acid</p> <ul style="list-style-type: none"> - They are less persistent in the environment - Mild health hazards to human and animals especially the herbicide and fungicide range. However, health risk is higher with insecticides 	They control pest by acting on the nervous system, interfering with the nerve impulse transmission, disrupting the enzyme cholinesterase that regulates acetylcholine, with enzyme effect usually reversible
4	Pyrethrin (synthetic version of Pyrethrin, modified to increase stability in the environment)	<ul style="list-style-type: none"> - <i>Lambda</i>-Cyhalothrin - Cypermethrin - Deltamethrin - Esfenvalerate - Permethrin 	Stable in sunlight (do not degrade quickly)	Disrupts nerve impulse transmission (increases sodium flow into axon), which stimulates nerve cells and eventually causes paralysis

Source: Adewunmi and Fapohunda (2018)

(vi) Organochlorine

Organochlorine pesticides (OCs) are hydrophobic organic compounds capable of accumulating in the organisms. In aquatic environments can enter into an organism including fish through two pathways, which are bio-concentration directly through the water environment (LeBlanc, 1995), and bio-magnification through food-web preys (Kiriluk, Servos, Whittle, Cabana & Rasmussen, 1995). Lipid content (Bentzen, Taylor & Mackay, 1996), depuration rates, size and exposure duration of the organism (Hording *et al.*, 1997), as well as the structure of the food web and the environmental concentrations of the chemicals are all potential factors influencing bioaccumulation of OCs in an aquatic organism. Pelagic organisms including prawns were found to be more subjected to OCs bioaccumulation than biota relying upon benthic primary production (Kidd *et al.*, 1998). The exposure of OCs in humans creates severe health hazards particularly breast cancer, testicular cancer, endocrine dysfunction, births defects, and lower sperm count (Garry, 2004). Chemical compounds such as DDT, HCH and Lindane that are environmentally pollutants and has been banned from use in farms in developed countries unfortunately remains in use (Carvalho, 2006). Most of the OCs were banned in 1970s for their long persistence in the environment but, they are still detectable in fish from various waterways (Zhang, Pan, Bai & Li, 2014). Examples of OCs are Aldrin, Chlordan, Dieldrin, Endosulfa and Endrin (Adewunmi & Fapohunda, 2018).

(vii) Organophosphorous

Organophosphorus (OPs) are one of the most commonly used pesticides for insect pest management. Most of these compounds have low persistence in aquatic ecosystems, but the relative lack of target specificity has raised concerns about their potential to cause adverse effects on non-target wildlife populations from estuarine and coastal areas (Matthiessen & Law, 2002). Despite the high efficiency, the widespread use of OPs results in the release of their residues into natural water, tending to be toxic to non-target organisms such as fish and many species of aquatic invertebrates (Liu, Yuan & Li, 2012). Fenitrothion (FS [O,Odimethyl- O-(3-methyl-4-nitrophenyl) phosphorothioate]) is an OP that has several applications in agriculture. Fenitrothion is employed to control insects on rice, cereals, fruits, vegetables, stored grains, and cotton (Zayed & Mahdy, 2008). Also, it is currently used for mosquito control (Delatte *et al.*, 2008). It is known that FS in water solution undergoes photo-degradation, resulting in the release of several toxic metabolites, some of which are more toxic to aquatic organisms than the parent compound (Zayed & Mahdy, 2008). Fenitrothion, like other OPs, is bio-activated by the mixed function oxygenase. Examples of

OPs are Chlorpyrifos, Dimethoate, Fenthion, Naled, Temephos, Trichlorfon (Adewunmi & Fapohunda, 2018).

(viii) Carbamates

The carbamate pesticides are most widely used for agricultural and residential applications. Enormous amount of these components, such as aldicarb, carbofuran, carbaryl etc., are used worldwide. The carbamates do not persist long in the environment, they rapidly degrading pesticides. However, they are also toxic to non-target organisms (Geraldine, Bhavan, Kaliasurthy & Zayapragassaran, 1999). Some of the degradation products of carbamates are more persistent than the parent component (Amiard, Caquet & Lagadic, 2000). Carbaryl has a depressive effect on mitochondrial respiration without affecting the phosphorylation complex (Moreno, Serafim, Olivei & Madeira, 2007). The toxic effect of pesticides are known to alter the behavioral pattern, growth, reproductive potential and susceptible to diseases of crustacean by affecting a variety of biochemical and physiological mechanisms (Ali, Mannan & Parween, 2007). Examples of carbamate pesticides are Carbaryl, Propoxur, Methomyl, Carbofuran, Thiodicarb, Barban, Prophan, Triallate and Nabam (Adewunmi & Fapohunda, 2018).

(ix) Pyrethrins

Pyrethroids are a class of neurotoxic pesticides, the use of which has been continuously increasing during the last two decades (Wolansky & Harrill, 2008). These compounds are derivatives and synthetic analogues of natural pyrethrins as it was reported by Hossain *et al.* (2005), and can be categorized in two types, based on structure-activity and symptomology (Anadón, Martínez-Larrañaga & Martínez, 2009). Wolansky and Harrill (2008) have reviewed a large number of studies showing behavioral alterations after pyrethroid exposure. In fact, these compounds are highly toxic to aquatic invertebrates, and even at non-lethal concentrations they are able to induce significant behavioral changes in aquatic invertebrates and affecting their survival (Sánchez-Fortún & Barahona, 2005). According to Wolansky and Harrill (2008), all pyrethroid compounds, regardless of species, are able to impair motor function that is the most extensively characterized neurobehavioral endpoint for pyrethroid effects. Examples of pyrethroids pesticides include *Lambda*-Cyhalothrin, Cypermethrine, Deltamethrine, Esfenvalerate and Permethrine (Adewunmi & Fapohunda, 2018). Pyrethroids are contained in agricultural insecticide, home applied insecticide. Maximum level of *Lambda*-cyhalothrin for prawns is 0.05 mg/kg (FAO/WHO, 2018). In human, *lambda*-

cyhalothrin causes damage to the lungs, nervous, birth defects and even cancer also dizziness, headache, nausea, lack of appetite, and fatigue and in severe poisonings, seizures and coma may occur (Basir *et al.*, 2011).

Several African studies have reported very poor pesticide handling practices and low risk awareness among farmers in general (Matthews, Wiles & Baleguel, 2003). This situation of not knowing of pesticide management is a serious threat to public health and can create environmental problems. In Tanzania variously study on pesticide residue have been done as it is described in (Table 4). Activities involved including rice farming and vegetables cultivation as is the most important activity in the northern part of the Rufiji delta, followed by fishing and sales of mangrove woods (Stadlinger, Mmochi, Dobo, Gyllbäck & Kumblad, 2011). It is only during the rain period from January to June that salinity conditions suitable for rice farming occur in the delta and a frequent use of pesticides to combat mangrove crabs in the mangrove rice farms in the Rufiji delta. Similarly, January to June is the high period of prawns season within the Rufiji delta and Bagamoyo (Mwevura, 2007). This has raised concerns of potential effects on human health and the estuarine environment. Number of pesticide residues including lindane, organophosphates, and metabolites of persistent organochlorines (Mwevura, 2007) have also detected in the surrounding environment of the rice farms. Fish and shrimp mortalities have been reported in the mangroves of Chwaka Bay that coincide with the application of pesticides and fertilizers on adjacent rice fields (Mwevura, 2007).

The level of toxicity by pesticides was classified by WHO into four categories. These include class one very toxic, class two toxic, class three slightly toxic and class four un harmful (Fattier, 2010). Again new techniques of the pesticide were introduced which are biological (chemical free) and include microbial pesticides, biochemical pesticides and genetically modified organisms (GMOs) to rescue the situation of high quantity spread of agro-chemicals in agricultural fields (Adewunmi & Fapohunda, 2018). Nevertheless, in the tropical regions of sub-Saharan Africa, the use of pesticides (agrochemicals) is still the common practice. For that matter persistent pesticide residues contaminate food and disperse in the environment. Food quality becomes compromised and the environment adversely affected.

But agricultural pesticides use contributes to environmental pollution However even at nonlethal doses, the chemicals disrupt the nervous system, liver, hormonal regulation,

reproduction, embryonic development and growth in fish including prawns (Barse, Chakrabarti, Ghosh, Pal & Jadhao, 2007; Palma *et al.*, 2009).

Table 4: Study on pesticide residues done in Tanzania

Study Area	Study topic/Aim	Pesticide residue	Pesticide residues concentration
Arusha: Ngarenanyuki Arumeru district	Residues of organochlorinated pesticides in Soil from Tomato Fields, Ngarenanyuki, Tanzania	Organochlorine	- Endosulfan sulphate 0.2407 mg/kg dw; Chlorpyrifos 0.1253 mg/kg dw; p, p'-DDE 0.1482 mg/kg dw; p, p'-DDD 0.154 mg/kg dw and Lindane 0.2126 mg/kg dw. (Kihampa <i>et al.</i> , 2010)
Lake Victoria: Mwanza, Sengerema, Geita, Ukerewe and Musoma	Pesticide residues in Nile tilapia (<i>Oreochromis niloticus</i>) and Nile perch (<i>Lates niloticus</i>) from Southern Lake Victoria, Tanzania	Organochlorine	- Fenitrothion 0.003 mg/kg - DDT 0.03 mg/kg - Endosulfan 0.2 mg/kg (Henry & Kishimba, 2006)
Coast Region Vikuge	Concentrations of pesticide residues in grasses and sedges due to point source contamination and the indications for public health risks, Vikuge,	Organochlorine	- Aldrin 11 ng/g fw - Dieldrin 8 ng/g fw - HCH 74 ng/g fw - DDT 7922 ng/g fw (Marco & Kishimba, 2005)
Northern Tanzania	Agrochemicals use in horticulture industry in Tanzania and their potential impact to water resources	Organophosphate and Nitrate	- Phosphates and nitrates in surface and ground water (Lema <i>et al.</i> , 2014)
Coast Region	Organochlorine pesticides and metabolites in young leaves of <i>Mangifera indica</i> from sites near a point source in Coast region, Tanzania	Organochlorine	- DDT 2.7– 649 ng/g - DDE 1–231 ng/g - DDD 0.5–55 ng/g - HCH 2 ng/g (Marco & Kishimba, 2007)

Source: (Stadlinger *et al.*, 2011)

2.8 Pollution in Tanzania

There are a number of studies on heavy metals in the marine environment in Tanzania. For instance, Hg, Pb and Cd; and pesticide residues including organochlorine residues Hexachlorobenzene, α -hexachlocyclohexane, *cis*-chlordan, *trans*-nonachlordane, *cis*-nonachlordane, *pp'*-DDE, *op'*-DDD, *pp'*-DDD, *op'*-DDT, and *pp'*-DDT have been reported in prawns above the maximum level recommended by WHO/FAO (Mdegela *et al.*, 2009). Most of the farmers, especially in studied areas such as Rufiji (Tanzania coastal mainland) and Cheju (Zanzibar) do not have adequate knowledge on the impacts and how to use the pesticides as prescribed by the manufacturers (Stadlinger *et al.*, 2011). Rumisha *et al.* (2016)

reported that mangrove ecosystems at Pangani, Wami, and Rufiji are threatened by Cr, Co, Cu, Fe, Mn, Ni, Hg, Pb, Cd and Zn from anthropogenic activities and erosion in the river catchments. Additionally, contamination of giant mud crabs (*Scylla serrate*) and giant tiger prawns *Penaeus monodon*) with trace metals of Cd, Cr and Pb was reported although did not exceed maximum limits for human consumption (Rumisha *et al.*, 2017).

Also there is large amount of domestic and industrial wastes released daily to the aquatic environment in Tanzania without prior treatment (Shilla, 2016). Higher concentrations of Pb, Cr, Cu, and Zn were reported in Malindi the coastal region of Zanzibar suggesting pollution in the area was due to anthropogenic activities. A similar study by (Shilla & Routh, 2018) around the Rufiji delta indicates of polycyclic aromatic hydrocarbon (PAH) contamination in the surface sediments were higher (127 – 376 ng/g) the sites as a result of fuel spills and contribution from terrestrial sources from different land use practices, such as agriculture, fishing, and harvesting firewood, charcoal, and mangroves poles.

Pesticide pollution status in the area where agricultural input is not intensively used appeared to be in very low level as compared to areas associated with agricultural pesticide use (Kishimba *et al.*, 2004). Dar es Salaam coast, Mahonda Makoba basin in Zanzibar and a former pesticide storage area at Vikuge Farm in Coast region levels of DDT in water, sediments and soil were up to 2 gL⁻¹, 700 gkg⁻¹ and 500 gkg⁻¹, respectively, while those of HCH were up to 0.2 gL⁻¹, 132 gkg⁻¹ and 60 gkg⁻¹, respectively (Kishimba *et al.*, 2004). The levels of pesticide residues in aquatic biota were much higher than those in the water most likely due to bioaccumulation.

Furthermore, Pb, As, Cd, Fe and Cu were detected in *Fenneropenaeus indicus* in Dar es Salaam City with concentration range of 1.173 – 2.325 mg/kg (Saria, 2016). In addition, As, Hg, Cr, Pb and Zn were also detected in fish from the Tanzanian coastal areas with higher mean concentrations of Hg (0.170.01 mg/kg) and Cr (23.70 mg/kg) (Bungala, Machiwa & Shilla, 2017). Similarly, high concentrations of Hg (0.06 mg/kg) were detected in fish from the Msimbazi Creek, Dar es Salaam and Cr (45.5 mg/kg) at Dar es Salaam port. Trace metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) were reported in sediments in the mangrove forests around the Rufiji delta in the southeastern coastal of Tanzania that was associated with urban development, agricultural activities in the catchment, and pollutants from upstream sections of the Rufiji river (Minu *et al.*, 2018). High concentration of heavy metals such as Aluminum (Al), Zn, iron (Fe), Cu, cobalt (Co), chromium (Cr), Cd and Pb were reported to be

discharged into the coastal area of Tanzania from agricultural, anthropogenic and industrial sources, which in turn pollutes marine ecosystems (Rumisha *et al.*, 2017).

Given the importance of such studies at controlling further pollution and safeguarding economic, social and health well-being of human populations, this study explored presence and sources of heavy metals and pesticides in prawns, water and sediments in Kibiti and Bagamoyo districts in Kilwa, Kisiju and Bagamoyo zones; areas that have limited information on the factors.

CHAPTER THREE

MATERIAL AND METHODS

3.1 Material

3.1.1 Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade. These was summarized in Table 5.

Table 5: Chemicals and reagents

Name of chemical/Reagent	Manufactures
Nitric acid (HNO_3) (69% - 72%) purity	Gato Perez, 33. 08181 Sentiment SPAIN. Tel. 34-937456400 Made in the European Union.
Sulphuric acid (H_2SO_4) 98% Extra pure	Loba Chemie Pvt. Ltd, 107 Wodehouse Road, Jehangir villa, Mumbai-400005. India
Hydrochloric acid (HCl) (37%) purity	Gato Perez, 33. 08181 Sentiment SPAIN. Tel. 34-937456400, Made in the European Union.
Perchloric acid (HClO_4) 70% purity	Gato Perez, 33. 08181 Sentiment SPAIN. Tel. 34-937456400 Made in the European Union
Anhydrous sodium sulphate (Na_2SO_4) (99%)	Sigma-Aldrich, Co. 3050 Spruce Street, St. Louis Mo 63103 USA.
Dichloromethane (CH_2Cl_2) 98% purity	Sigma-Aldrich, Co. 3050 Spruce Street, St. Louis Mo 63103 USA.
Cyclohexane (C_6H_{12}) 99% purity	Sigma-Aldrich, Co. 3050 Spruce Street, St. Louis Mo 63103 USA.
Ethyl acetate ($\text{CH}_3\text{COOCH}_2\text{CH}_3$) 99% purity	Sigma-Aldrich, Co. 3050 Spruce Street, St. Louis Mo 63103 USA
Sodium chloride (NaCl) 99.5% purity	Sigma-Aldrich, Co. 3050 Spruce Street, St. Louis Mo 63103 USA

Source: (Lab reagents, 2018)

Table 6: Laboratory equipment

Name of Equipment		Modal and Manufacture
High-density polyethylene bottles		S/N301675-0016 Made in china
Membrane filters		0.45 µm GF/C Amicon, USA
Cooler Box		Made in China
Polyethylene bottles,		DWK Life science (Kimble), USA
Stainless steel scissors		Sci Labs, USA
Mortar with a pestle		GSC International Inc USA
Desiccators		United scientific supply, USA
Hot plate		Hotplate, CB500. Made from Germany
Sieved with a 1 mm sieve		S/N 352710, Endecott LTD, London England
Whatman filter paper		Amicon, USA
50 mL volumetric flask		DWK Life science (Kimble), USA
Beaker		Wilma-Lab glass, Thomas Scientific , Swedesboro, NJ 08085 USA
Atomic absorption spectrophotometer (AAS)		Model GFA-EX7i, Shimadzu Corporation Made in Japan
Analytical balance		S/N 8332140269 Made in China
Furnace		DMA-80, Milestone srl, Italy
Direct Mercury Analyzer		DMA-80, Milestone srl, Italy.
Separating funnel		Wilma-Lab glass Thomas Scientific , Swedesboro, NJ 08085 U.S.A
Rotary evaporator		RE – 5002, Shangai, China)
Gas chromatography spectrophotometer (GC-MS)	mass	GC-MS 2010 Plus Shimadzu, Japan

Source: (Lab equipment, 2018)

3.1.2 Sample collection

Prawns, sediments and water were collected from seven sampling sites (villages) which are; Kikale and Nyamisati (Kisiju zone), Ruma and Mbvera (Kilwa zone), Kisutu, Dunda and Magomeni in Bagamoyo zone during prawns harvesting season on May and June, 2018.

3.2 Decontamination procedures

All equipment used were washed thoroughly by using detergent, then rinsed with distilled water and the rinsed again with deionized demineralized water, then kept to dry in the tray in the oven at 60 °C to destroy all the harmful substances presence in the equipment.

3.3 Methods

3.3.1 Study area

This study was conducted in Bagamoyo and Kibiti districts of the Coast region of Tanzania whereby Bagamoyo, Kisiju and Kilwa are the richest prawn fishing zones. The zones were selected because they are characterized with potential prawns fishing and they contribute about 25 - 45% of the total annual prawn catches in Tanzania (PMP, 2012). Seven villages in the three zones were selected for this study. In Bagamoyo zone (Dunda, Magomeni, and Kisutu), Kilwa zone (Ruma, and Mbwera) and Kisiju zone (Nyamisati and Kikale) villages (Fig. 2).

The dominant prawn species in the zones are *Penaeus indicus* and *Metapenaeus monoceros* (Bagamoyo - Zone 1) and Kisiju (Zones 2), and *M. monoceros*, *P. semisulcatus* and *P. indicus* (Kilwa - Zone 3). Bagamoyo receives fresh water from Ruvu; Wami and Pangani rivers, while Kisiju and Kilwa receives fresh water from Rufiji river.

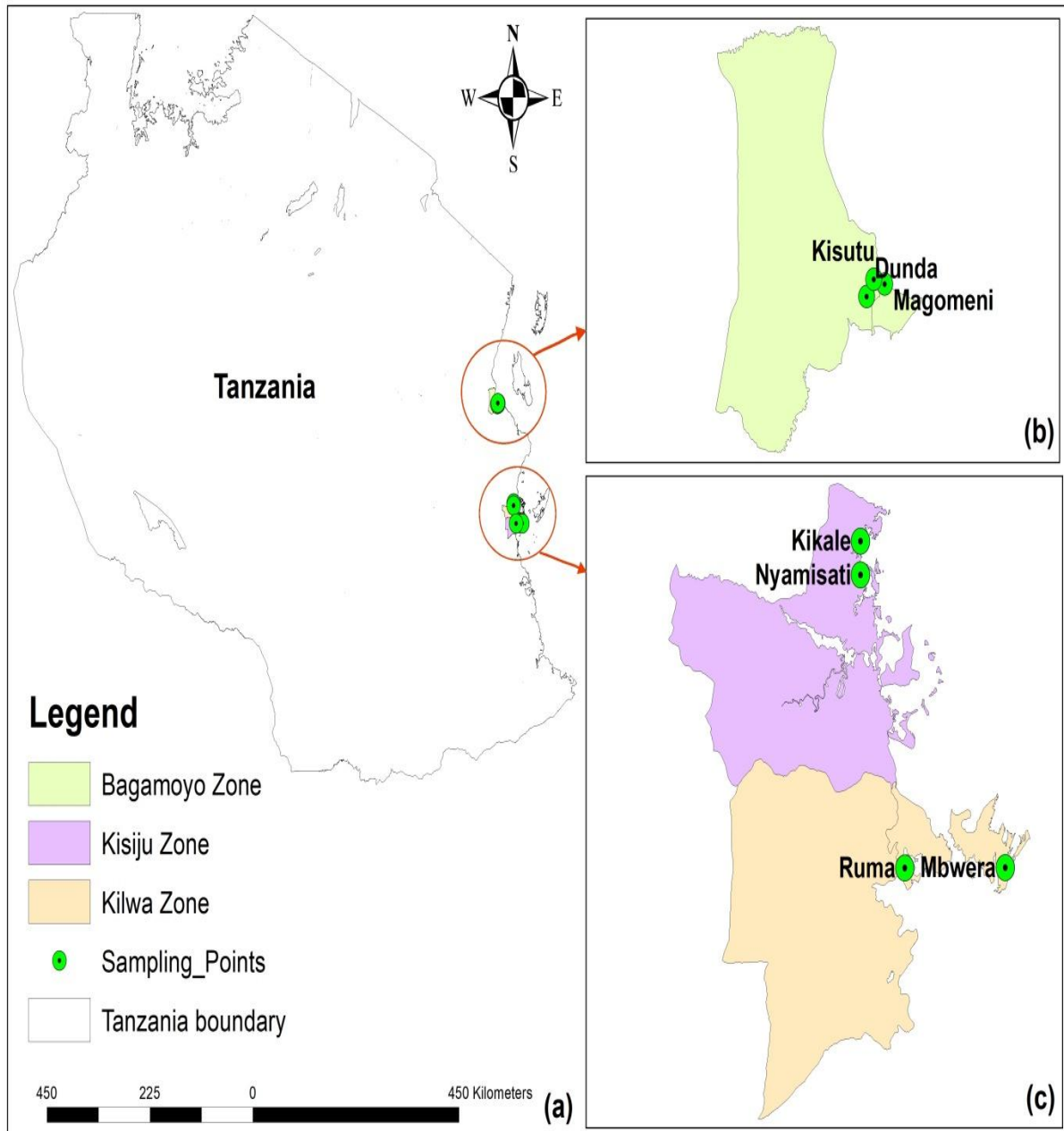


Figure 2: A map of Tanzania showing sampling points in the prawns fishing zones of Bagamoyo, Kisiju and Kilwa along the Indian Coastline of Tanzania

3.3.2 Study design

A cross sectional study design was adopted, this method is often used to make inference about possible relationships or to gather preliminary data to support further research and experimentation. Samples were collected during the prawns' harvested season of the year.

Seven villages involved in this study were randomly selected from the two districts of Bagamoyo (Kisutu, Dunda and Magomeni) and Kibiti (Kikale, Nyamisati, Ruma and Mbwera). Information about sources of aquatic pollutants was also collected from the fishermen in the study zones by using structured questionnaire.

3.3.3 Sample size

(i) Respondents selection

All 126 respondents (including fishermen, farmers, fish traders, government officers) were selected using the following formula;

Total population = 54511 whereby 4800 (= 9%) are prawns fishers (MLDF, 2015)

$$N = \frac{Z^2 \times P(1-P)}{e^2} \text{ where } P = 0.09, e = 0.05 \text{ and } Z = 1.96$$

$$= \frac{1.96^2 \times 0.09 \times (1-0.09)}{0.0025} = 126 \text{ respondents (Charan \& Biswas, 2013)}$$

3.3.4 Data collection tools

(i) Questionnaire

Out of 126 respondents, 106 gave response from the structured questionnaires. That is, 18 respondents from each village were randomly selected and interviewed using a structured questionnaire.

(ii) Interviews

Face-to-face interviews (with structured questions) with District Environmental Officer and Agricultural Extension Officer was conducted. The officers were used as key informants for this study. Thus a total of 128 respondents were used in this study.

3.3.5 Collection of samples

Samples of water, sediments and prawns were collected from seven sampling sites (Kikale, Nyamisati, Mbwera, Ruma, Kisutu, Magomeni and Dunda) villages along the coast district of Bagamoyo, Kibiti along the prawns fishing zone of Kilwa, Kisiju and Bagamoyo (Fig. 2). Sampling sites were selected based on, accessibility and proximity to anthropogenic discharge sites, agricultural activities and highly prawns fishing zone. Samples were collected in triplicate therefore the total of 63 samples were collected, prawn (n=21), sediments (n= 21) and water (n = 21) (Ali *et al.*, 2016).

(i) Water

One (1 L) of sub-surface water samples were collected by hand grab method in triplicate approximately 10 cm below water surface from each sampling site. The samples was placed in labeled pre-cleaned high-density polyethylene bottles, and about 500 mL from each 1 L of collected water, were placed in labeled 1 L pre cleaned amber glass bottles, preserved with 10% NaCl filled up to the seal, leaving no space for air bubbles special for pesticide residue determination. The remaining 500 mL samples was for heavy metal determination, the samples was placed in the cool box equipped with ice bags for storage before transporting to laboratory for filtration and analysis (Kishimba *et al.*, 2004). In the laboratory, water were filtered through 0.45 μm GF/C membrane filters and then filtered samples for heavy metal determination were immediately acidified with 0.1 N HNO_3 (Wilken & Hintelmann, 1991). All glassware were washed with detergent, rinsed with double distilled water, soaked in 10% HNO_3 for 24 h and rinsed with double distilled water (Sarkar *et al.*, 2016).

(ii) Sediments

Surface sediments (approximately 10 cm) were taken using a hand corer in triplicate in different location within the sampling site. About 40 g of sediments were taken from each sampling location. The retrieved sediment cores were placed in acid-cleaned and rinsed with double distilled water polyethylene bottles, stored in the cool box equipped with ice bags and transported to the laboratory. In the laboratory, the sediment samples were frozen at $-20\text{ }^{\circ}\text{C}$ and stored for 48 h according to descriptions given in (Shilla, 2016) before further processing.

(iii) Prawns

Fifty (50 g) of Prawn samples were collected in triplicate from open markets in sampling location during low tide, stored in cool boxes with ice cubes and immediately transported to the laboratory and stored at $-20\text{ }^{\circ}\text{C}$ for 3 days before further processing according to (Rumisha *et al.*, 2016).

3.3.6 Sample preparation for heavy metal (Pb, Cd and Zn)

(i) Sediments

Fifteen (15 g) of sediments sample was thawed, about 10 g weighed and dried in an oven at $80\text{ }^{\circ}\text{C}$ until a constant weight was observed, and then grounded with mortar and pestle, sieve

(aperture size was 125 μm , diameter was 200 mm) and preserved in desiccator (circular made of heavy glass, lower compartment contain lump of silica gel) (Ali *et al.*, 2016).

(ii) Prawns

Fifteen (15 g) of prawn samples were thawed, washed several times with double distilled water, rinsed with double deionized water then sliced into small pieces with stainless steel scissors, the non-edible parts removed, weighed and recorded. Then 10 g of prawn samples were dried in an oven at 80 °C until a constant weight was observed, and then the dried samples were finely pulverized in a carbide mortar with a pestle, sieved (aperture size was 125 μm , diameter was 200 mm, frame was made by brass and mesh was made by stainless steel) and preserved in polyethylene bags and kept in desiccators (Sarkar *et al.*, 2016).

3.3.7 Sample digestion for heavy metal (Pb, Cd and Zn)

(i) Water

Hundred (100 mL) of water sample was placed in 250 mL beaker with 10 mL HNO_3 and 10 mL HCl . When the water stopped reacting with acids, the mixture was heated in a hot plate at 60 °C for 30 min until brown fumes were formed. The mixture was allowed to cool at room temperature and 10 mL of HClO_4 was added and then re-heated for 5 min and allowed to cool. The content from the beaker was then transferred to 50 mL volumetric flask and diluted to the mark with deionized water and then filtered by using 125 μm Whatman filter paper (Amicon, USA) (Sarkar *et al.*, 2016).

(ii) Sediments

Two (2 g) of dry weight sediments was placed in a 250 mL beaker with a solution of 10 mL HNO_3 and 10 mL HCl . When the sediments stopped reacting with acids the mixture was heated in a hot plate at 60 °C for 30 min. After cooling at room temperature, 10 mL of HClO_4 was added and re-heated at 100 °C for 5 min and then allowed to cool at room temperature. The mixture was then transferred to 50 mL volumetric flask and diluted to the mark with deionized water and filtered with a 125 μm Whatman filter paper (Amicon, USA) (Ali *et al.*, 2016).

(iii) Prawns

Five grams of dry weight prawns powder was placed in a 250 mL beaker with a solution of 5 mL concentrated HNO₃ and 5 mL concentrated H₂SO₄. When the prawn's tissue stopped reacting with acids the mixture was heated in a hot plate at 60 °C for 30 min. the mixture was cooled at room temperature and 10 mL of HNO₃ (65%) was added and re-heated slowly to 120 °C. The temperature was increased to 150 °C and the mixture was removed from the hot plate when the sample turned black. The mixture was then allowed to cool at room temperature and 30% H₂O₂ was added until the sample became clear. Then the content from the beaker was transferred to 50 mL volumetric flask and diluted to the mark with deionized water , and filtered with a 125 µm Whatman filter paper (Amicon, USA) then was preserved in plastic container (Sarkar *et al.*, 2016), with slight modification.

3.3.8 Heavy metal quantification

All samples were analyzed for Pb, Cd and Zn by an Atomic Absorption Spectrophotometer (AAS) (Model GFA-EX7i, Shimadzu Corporation, Japan) using an air acetylene flame with digital read out system. The limits of detection for heavy metals were set at Pb: 0.01 mg/L, Cd: 0.001 mg/L and Zn: 0.01 mg/L. The cathode lamps used were of Pb (217.0 nm, lamp current 5.0 mA), Zn (213.9 nm, lamp current 5.0 mA) and Cd (228.8 nm lamp current 4.0 mA).

(i) Method performance

All analyses were done in triplicated to assess the reproducibility of measurements. The accuracy of analysis was verified by analyzing the certified reference materials. Dogfish (*Squalus acanthias*) liver DOLT-3 (National Research Council, Canada) was used as a certified reference material (CRM) for prawns, for sediments 2 certified reference materials (CRM) and 2 contained only aqua regia solution (blanks), River clay sediments LGC639 (Laboratory of the Government chemist, United Kingdom) and for water Estuarine Water NRCC-SLEW-1 was used as CRM from International Atomic Energy Agency (IAEA). Blanks and calibration standard solutions were also analyzed through the same method. The recoveries for sediments were Cd 100%, Pb 92% and Zn 95%, for prawns were Cd 87%, Pb 92% and Zn 95% and for water recoveries were Cd 95%, Pb 97% and Zn 99%.

3.3.9 Mercury quantification

Mercury determination was done by using Direct Mercury Analyzer-80 (DMA). The solution used for cleaning and decontamination of vessels and crucible was prepared using ultrapure water.

All equipment including vessels and crucible used were decontaminated by washing with a common detergent rinsing with ultra-pure water three times and soaking into a diluted HNO₃ 20% (v/v) bath for 24 h at 25 °C. Each soaking was followed by an intensive rinsing with ultra-pure water then dried in clean environment and preheated at 750 °C in a furnace for 4 h to avoid contamination. The calibration standard was prepared by making two appropriate dilutions in stock water solution (1000 mg/L) of Hg⁺ in 2% HNO₃. A blank calibration solution was also used for a zero calibration (Maggi *et al.*, 2009)

The samples of prawns, sediments of approximately 0.1935 g and 0.1464 mL of water in triplicates were used. The mass of the samples were then transmitted into the test unit. The test process was started after weighing all the samples. The analyses were carried out with a Direct Mercury Analyzer (DMA-80, Milestone srl, Italy). The sample Hg determination was dried and then thermally decomposed by controlled heating. Decomposition products are carried to a catalyst by an oxygen flow, then sample oxidation was completed and halogens and nitrogen/sulphur oxides were trapped. The final decomposition products were passed through a mercury amalgamator which collects Hg. The Hg amalgamator was heated to 700 °C and the Hg was released and quantified (Roy & Bose, 2008).

(i) Method performance

The DMA-80 instrument was calibrated in the low (0 - 50 ng) and high (50 - 500 ng) concentration ranges for the low and high values of mercury in samples. The calibration range automatically switched over depending on the concentration in the unknown samples. Before performing calibration the instrument was run several times with empty boats to obtain a very low and stable absorbance value (0.0010). After a stable low value had been obtained, calibration was performed and samples were weighed. For low range calibration, four aliquots were used, (0.0163 g, 0.0275 g, 0.0290 g and 0.0297 g) and for the high range calibration (0.0976 g, 0.0704 g, 0.0835 g and 0.0808 g) were taken in different quartz boats. Dogfish (*Squalus acanthias*) liver DOLT-3 (National Research Council, Canada) was used as a Certified Reference Material (CRM) for prawns, for sediments 2 certified reference

materials (CRM) and 2 contained only aqua regia solution (blanks), River clay sediments LGC639 (Laboratory of the Government Chemist United Kingdom) and for water Estuarine Water NRCC-SLEW-1 was used as CRM from International Atomic Energy Agency (IAEA). Two sets of samples were placed in the auto sampler. Each sample was processed with the following instrumental parameters: (a) drying 60 s, 300 °C, (b) decomposition, 120 s, 850 °C and (c) waiting time 45 s. Limits of detection set was 0.001 mg/L, percentage recovery was 95% and wavelength was, 253.7 nm (Roy & Bose, 2008).

3.3.10 Pesticide residues analysis

All the reagents and solvents used in this study were of analytical grade (99% purity). All stock solutions were stored at 4 °C. All working solutions were made immediately prior to use. Working standard solutions were made by diluting stock standards and mixtures of standards of different concentrations were used in most cases for the screening of the pesticide residues.

(i) Water extraction

Five hundred milliliter of water was placed in a separating funnel and shaken with 25 mL of CH₂Cl₂. The organic layer was separated and the process was repeated three times. Ten grams of anhydrous Na₂SO₄ was added to dry the extract. The CH₂Cl₂ was removed by rotary evaporator until 2 mL of the extract was left according to Kishimba *et al.* (2004) with slight modification.

(ii) Sediments extraction

Sediment samples were thawed, weighed and then 10 g of sediments was mixed with 10 g of anhydrous Na₂SO₄ that was continually added until the sample flowed freely. The mixture was placed in a glass stoppered bottle and 50 mL of CH₂Cl₂ were added. The sample was sonicated for 20 mn and then filtered and evaporated using rotary evaporator until the final volume was 2 mL Kishimba *et al.* (2004) with slight modification.

(iii) Prawns extraction

Thirty grams of wet prawns sample were thawed, weighed and about 10 g were taken from the grounded one and extracted with dichloromethane (20 mL) and the solvent evaporated in vacuo, after which the extract was dissolved in cyclohexane (3.5 mL). Part of the extract (2

mL) was transferred to a tarred vial and kept in a hood to evaporate the solvent (Kishimba *et al.*, 2004).

(iv) Clean up

Water extracts in all cases were deemed sufficiently clean and were thus not subjected to clean up procedures. Each filtered sediment extract was concentrated and the solvent changed to cyclohexane, ethyl acetate (1:1 v/v, 2 mL). The extract (1 mL) was cleaned up by Size Exclusion Chromatography (SEC; Biorad SX-3, ethyl acetate, cyclohexane 1:1 v/v as eluent), and the appropriate fraction was collected. This was later concentrated and the solvent changed to cyclohexane, acetone (9:1 v/v, 2 mL) for GC-MS (GC-MS 2010 Plus Shimadzu, Japan) analysis. The prawns and water sample extracts were cleaned by SEC as above (Kishimba *et al.*, 2004) with slight modification.

(v) Pesticides analysis and quantification

The final extract of prawns, water and sediments were analyzed for pesticide residues using Gas Chromatography-Mass Spectrometry (GC-MS 2010 Plus Shimadzu, Japan) operating in Electron Ionization (EI) mode (MS) at 70 eV and Flame Ionization Detector (FID) for GC. A Restek-5MS column (30 m x 0.25 mm x 0.25 μ m) was used. The temperature was maintained at 90 °C for 2 min at the beginning then raised to 260 °C for 5 min at the rate of 35 °C per min. The injection temperature was 250 °C with split less injection mode whereas injection sample volume was 1 μ L. The flow rate of a carrier gas, Helium was 1.21 mL/min. The ion source temperature and interface temperature in MS were 230 °C and 300 °C, respectively. The pesticide residues were identified by scan method, which involves the use of Mass Spectral Library and Search Software (NIST). Quantification of pesticide residues in the samples was done using Peak Integration method where by ion allowance was 20% (Kishimba *et al.*, 2004) with slight modification.

(vi) Method performance

Blank and recovery experiments were run for all three samples using standard methods (Åkerblom, 1995). For recovery experiments, pesticide mixtures in acetone were added to the pesticide-free matrix. Spiked prawns, water and sediment samples were stored cold overnight before extraction. In most cases the recoveries of the detected pesticides ranged from 75-92%, these were within the ranges and the results were not corrected according Kishimba *et*

al. (2004) with slightly modification. The limits of detection were 0.001 mg/L in water, 0.001 mg/kg sediment (dry weight), and 0.01 mg/kg prawns (fresh weight).

3.4 Data analysis

Statistical analysis of data was done in SPSS (IBM SPSS, Version 21, 2012). Data on the stakeholders perception on sources of aquatic pollution was analyzed and descriptive statistics was used to compare the responses of respondents. Software R version 3.5.0 for Windows (R Development Core Team 2018), Turkey HSD package was used to analyze mean separation for the pair of variables that showed statistical difference. In order to obtain mean values, standard errors and confidence levels, a one-way ANOVA was used to compare the heavy metal concentrations between sampling locations (Zones). The different statistical methods were performed with a 95% confidence interval (significance, $p < 0.05$).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Demographic characterization

Demographic characterization of the fishing zones is as shown in Table 7. Most of the respondents were fishermen (52.5%), followed by peasants and businessmen. Men were more actively engaged in fishing activity, within the age group of 30 – 39 and 40 – 49 years, whereas most of them attained primary education level (Table 7).

Table 7: Demographic characteristics of respondents in the prawns fishing zone

Attributes	n (%)	Cumulative percent
Gender		
Man	102 (83.6)	83.6
Woman	20 (16.4)	100
Marital status		
Un-married	10 (8.2)	8.2
Married	96 (78.7)	86.9
Separated	12 (9.8)	96.7
Divorced	2 (1.6)	98.4
Widow	1 (0.8)	99.2
Un-marriage	1 (0.8)	100
Age		
10-19	1 (0.8)	0.8
20-29	21 (17.2)	18.2
30-39	28 (23.0)	41.3
40-49	29 (23.8)	65.3
50-59	24 (19.7)	85.1
60-69	12 (9.8)	95.0
70-79	6 (4.9)	100.0
Education level		
Uneducated	17 (13.9)	13.9
Primary	90 (73.8)	87.7
Secondary	15 (12.3)	100
Occupation		
Fishermen	64 (52.5)	52.5
Peasants	44 (36.1)	88.5
Businessman	12 (9.8)	98.4
Others	2 (1.6)	100.0
Total	122 (100)	100.0

Fishing activity was mostly done around the mangrove, rivers, shallow sea, and deep sea, mostly once a day. The prawn catch per day for some prawn fishers was either < 10 kg (31.1%) or < 50 kg (29.5%) respectively. However, a 77% decline in prawns yield was also

observed. The fishing methods employed in the study areas was the use of gillnets, ring nets and pins with average net size of 3 inches (Table 8).

Table 8: Socioeconomic activities around the fishing zones

Attribute	n (%)	Commulative (%)
Any agricultural activities around the area		
Yes	97 (79.5)	79.5
No	21 (17.2)	96.7
I don't know	4 (3.3)	100.0
Sizes of agricultural activities		
Small	37 (30.3)	30.3
Medium	46 (37.7)	68.0
Large	13 (10.7)	78.7
Not applicable	26 (21.3)	100.0
Types of crop harvested		
Rice	79 (64.8)	64.8
Maize	8 (6.6)	71.3
Cassava	5 (4.1)	75.4
Tomatoes	2 (1.6)	77.0
Cashew nuts	1 (0.8)	77.9
Vegetables	1 (0.8)	78.7
Not applicable	26 (21.3)	100.0
Any Industrial activities		
Yes	9 (7.4)	7.4
No	104 (85.2)	92.6
I don't know	9 (7.4)	100.0
Fishing location		
Rivers	22 (18.0)	18.0
Estuaries	2 (1.6)	19.7
Mangrove	42 (34.4)	54.1
Deep sea	12 (9.8)	63.9
Shallow sea	19 (15.6)	79.5
<i>Mwamba</i>	9 (7.4)	92.5
All	16 (13.1)	100.0
Prawns catch per day (kg)		
< 10	38 (31.1)	31.1
< 30	29 (23.8)	54.9
< 50	39 (29.5)	84.4
> 50	19 (15.6)	100.0
Types of fishing gears		
Gillnet	96(78.7)	78.7
Ring net	18(14.8)	93.4
Pin	8(6.6)	100.0
Size of the nets (Inches)		
1	1(11.5)	11.5
2	67(54.9)	66.4
3	6(4.9)	71.3
I don't know	35(28.7)	100
Frequency of fishing prawns (day)		
Once	84 (68.9)	68.9

Attribute	n (%)	Commulative (%)
Twice	32 (26.2)	95.1
Above twice	6 (4.9)	100.0
Status of prawns yield		
Decline	94 (77.0)	77.0
Raised	17 (13.9)	91.0
Same	11 (9.0)	100.0
Total	122 (100)	100.0

Fishing, particularly prawn fishing was among the economic activities of socioeconomic importance to the coastal communities. Artisanal fishing is a pillar to most coastal livelihood households thus calling for proper management of the fisheries resource (Hamidu, 2014). The marine fishery is very important for coastal population as their major sources of daily income and food for their families (Mkama *et al.*, 2013). From the current study, majority of men (30 – 49 years) engaged in fishing activities were fishermen by occupation. Similarly (Okayi, 2013) observed more men (21 – 40 years) involvement in fishing activities with higher education level (secondary and tertiary) as opposed to most with low (primary) education level in this study. The age group and education levels of the respondents in the study zones suggest that majority were engaged in fishing activities immediately after completing their primary education. Level of education has been shown to have an impact on illegal fishing methods (dynamite and chemicals uses) on ecosystem and human health (Katikiro, 2014). Besides, the current study did not assess the impact of level of education on fishing practices.

4.2 Stakeholder perception on sources of aquatic pollution

Fertilizers, pesticides and herbicides were reported by the interviews to be the possible sources of aquatic pollution in the area. UREA, Booster, and NPK were the most commonly used fertilizers around the area. Also, a number of pesticides (*Karate*, and *Ninja*) and herbicides (*Roundup*, and *Weedall*) were commonly used as agricultural inputs (Table 9). Other than fishing, about 79.5% of agricultural activities were conducted in the area mainly rice farming. Farm sizes were of small and medium scale respectively (Table 8). Ongoing use of agricultural inputs nearby prawns nursery and farming areas may contribute to chemical contaminants which deposits during heavy rainfalls and floods to the estuaries and ultimately to the ocean.

Table 9: Agricultural inputs used in the study area

Attribute	N (%)	Cumulative (%)
Fertilizers		
UREA	38 (31.1)	31.1
NPK	10 (8.2)	39.3
Booster	26 (21.3)	60.7
Nil	48 (39.3)	100.0
Herbicides		
Roundup	41 (33.6)	33.6
Commander	8 (6.6)	40.2
Weedall	15 (12.3)	52.5
Herbicide	10 (8.2)	60.7
Nil	48 (39.3)	100.0
Pesticides		
<i>Karate</i>	38 (31.1)	31.1
<i>Ninja</i>	20 (16.4)	47.5
<i>Rungu</i>	3 (2.5)	50.1
<i>Cyberdip</i>	7 (5.7)	55.7
Commander	5 (4.1)	59.8
Nil	49 (40.2)	100.0
Total	122 (100)	100.0

Unexpectedly, fishing using chemicals (*Cyberdip* and *Utupa* a mixed herbs extract), and dynamites (18.9%) were practiced in the areas (Table 10). Agricultural activity, largely medium and small scales is heavily dependable by the local communities for their livelihood (Table 8). A routine usage of fertilizers, pesticides and herbicides as farming inputs in addition to industrial activities may have resulted into high concentration of marine pollutants, of which contaminates fish and marine environment. Likewise, according to Odada *et al.* (2004), industrial activities, disposal or incineration of waste, certain agricultural and the use of fertilizers, anti-parasites and feeds containing metals as well as natural causes have been reported to be sources of aquatic pollution. Heavy rains and floods carry agricultural waste deposits and residues of pesticide into the oceanic waters (Nzung'a, 2018). A decline in prawns production around the delta has been linked to agriculture activities that disturb spawning grounds of prawns (Mmochi & Francis, 2003). Similarly, Slade and Kalangahe (2015) reported dynamite fishing along the coastline of Tanzania to be detrimental not only to the environment but also to consumers. Dynamite fishing has been reported to destroy coral reefs that destruct spawning grounds of fish (Wells, 2009). The decreases in abundance and biomass of fisheries resources, and prawn in particular is in line with decline

of target species in various areas throughout the tropics (Hamidu, 2014). Likewise, a decline (77%) in prawn's yield was also reported in this study

Table 10: Chemicals used in illegal fishing in the study areas

Chemicals	n(%)	Cumulative (%)
<i>Utupa</i>	8 (6.6)	6.6
<i>Cyberdip</i>	9 (7.4)	14.0
Bottles of oxygen gas	2 (1.6)	15.6
Théoden	1 (0.8)	16.4
Not applicable	96 (78.7)	95.1
I don't know	6 (4.9)	100
Dynamite fishing		
Yes	23 (18.9)	18.9
No	99 (81.1)	100.0
Total	122 (100)	100.0

4.3 Pesticide residues

To ascertain presence of active ingredients in the pesticides and herbicides frequently used, a further analysis was done (Table 11). *Lambda*-cyhalothrin was the only active ingredient present in *Karate* and *Ninja* as indicated in the labeling. Other active ingredients from Herbicides, Weedall and *Cyberdip* are as shown in Table 11, however were not detected as pesticide residues in the study zones. *Lambda*-cyhalothrin is the active ingredient in several brand name products also, which include Warrior, Scimitar, Karate, Demand, Icon, and also Matador (He *et al.*, 2008).

Table 11: Presence of active ingredient in the pesticides/herbicides from the fishing zones

No	Herbicide/Pesticide	Active ingredient	Present/Absence
1.	<i>Karate</i> (<i>Su Karatii</i>)	<i>Lambda</i> -cyhalothrin	Present
2.	<i>Ninja</i>	<i>Lambda</i> -cyhalothrin	Present
		Imazamox,	Absent
3.	Herbicide	Halosalphone	Absent
4.	Weedall	Sapropylamine salt of glyphosate	Absent
5.	<i>Cyberdip</i>	Cypermethrin	Absent

Only *lambda*-cyhalothrin, an active ingredient in *Karate* and *Ninja* (Table 11) was detected as a pesticide residue in prawns and sediments (Table 12 and Table 13). A significant variation ($p < 0.05$) in *lambda*-cyhalothrin levels between zones was observed. *Lambda*-cyhalothrin level in prawn was detected in order of Kisiju > Kilwa and Kisiju > Kilwa > Bagamoyo in sediments. Besides, *lambda*-cyhalothrin residue was not detected either in prawns from Bagamoyo nor water samples from the three zones (Table 14). Absence of

pesticide residues in water might be contributed with ocean water drifts wash outs, agricultural seasonality and the residues tendency of settling down (Alegria & Shaw, 1999). *Lambda*-cyhalothrin is a pyrethroid insecticide He *et al.* (2008) which can bioaccumulate and not able to dissociate in the environment under suitable conditions. *Lambda*-cyhalothrin is an active ingredient of *Karate* and *Ninja* used in pests control. With intensive rice farming (64.8%, Table 8) around the fishing zones (Rufiji Delta), *Karate* and *Ninja* (*lambda*-cyhalothrin) are applied to control pests. Therefore, *lambda*-cyhalothrin contamination in prawns and sediments is suggested to originate from pesticide application from rice farms and its inability to dissociate in environment. According to Senoro *et al.* (2016), pesticide application is the most common method of controlling pests and weeds in rice and vegetable farming. Pesticides can migrate from treated fields to air, nearby land areas and water bodies. Also, pesticide residues may drain this is according to Owa (2014) through spray, runoff, and sink down into sediments caused by upwelling (Alegria & Shaw, 1999). *Lamba*-cyhalothrin has been reported to be highly toxic to freshwater shrimp and *Tilapia* fingerling Senoro *et al.* (2016) with a LC₅₀ in shrimp 0.28 µg/L (Wang *et al.*, 2007). Maximum acceptable level of *lambda*-cyhalothrin for prawns is 0.05 mg/kg (CAC, 2006). From the study, concentration of *lambda*-cyhalothrin in prawns from Kisiju and Kilwa was 5.6 to 45.2 folds above the acceptable levels. Fisheries resources, particularly smaller ones including prawns are very susceptible to *lambda*-cyhalothrin. Therefore, detection of *lambda*-cyhalothrin residue above acceptable level in prawns may indicate risks to human health.

The maximum acceptable level of *lambda*-cyhalothrin in sediments is 0.00372 mg/kg Wu *et al.* (2011). Again, concentration of *lambda*-cyhalothrin in sediments was 175, 4070 and 4432 folds above the acceptable limit in Bagamoyo, Kilwa and Kisiju respectively. On the other hand He *et al.* (2008) detected *lambda*-cyhalothrin in a range from 0.003 to 0.315 µg/g. Effect of *Lambda*-cyhalothrin in human including damage to the lungs, nervous, birth defects and even cancer also dizziness, headache, nausea, lack of appetite, and fatigue and in severe poisonings, seizures and coma may occur (Basir *et al.*, 2011)

Table 12: *Lambda*-cyhalothrin concentration in sediments in the fishing zones

Zones	Concentration (mean; mg/kg)	SD (mg/kg)	Maximum acceptable limit (mg/kg)	Limit of detection (mg/kg)	P-values
Bagamoyo	0.65	0.82			
Kilwa	12.21	3.24	0.00372	0.001	0.014
Kisiju	16.49	2.36			

Mean ±SD, (n=3), Means between the zones are significant at p < 0.05.

Table 13: *Lambda*-cyhalothrine concentration in prawns in the fishing zone

Zones	Concentration (mean; mg/kg)	SD (mg/kg)	Maximum acceptable limit (mg/kg)	Limit of detection (mg/kg)	P-values
Bagamoyo	nd				
Kilwa	0.28	0.40	0.05	0.01	0.017
Kisiju	16.49	2.36			

nd: not detected; Mean \pm SD, (n=3), Means between the zones are significant at $p < 0.05$.

Table 14: *Lambda*-cyhalothrin levels in water in fishing zones

Zones	Concentration (mean; mg/kg)	SD (mg/kg)	Maximum acceptable limit (mg/kg)	Limit of detection (mg/kg)	P-values
Bagamoyo	nd				
Kilwa	nd		0.01	0.001	0.017
Kisiju	nd				

nd: not detected; Mean \pm SD, (n=3),

4.4 Heavy Metals

The concentration of Pb, Zn, Cd and Hg in prawns, water and sediments varied widely in the three zones (Table 15). Heavy metal concentration in prawns in all zones was in a range between 24.29 – 24.91, 107.16 – 166.06, 0.18 – 1.17, and 0.05 – 0.19 mg/kg for Pb, Zn, Cd and Hg respectively. In sediments, the range for Pb, Zn, Cd and Hg was between 28.13 – 35.07, 133.44 – 153.49, 1.50 – 1.80 and 0.04 – 0.05 mg/kg respectively. For water, the range was between 0.05 – 0.74, 0.42 – 0.53, 0.02 – 0.09 and 0.03 – 0.19 mg/L for Pb, Zn, Cd and Hg respectively (Table 15). Generally, heavy metal concentration in prawns and sediments were detected in order of Zn>Pb>Cd>Hg, and Pb>Zn>Cd>Hg in water respectively. Furthermore, all the samples exhibited highest Zn concentration in the order of Kilwa>Kisiju>Bagamoyo. On the other hand, Hg exhibited lowest concentration in both prawns, sediments and water respectively. Besides, significant low levels of Pb, Zn and Cd were observed in all water samples. Zinc in prawns and water exceeded the FAO and WHO. (2015) acceptable maximum limit of 100 mg/kg for prawns according to Choi (2011), and 0.0766 mg/L for water, but it was below the acceptable limit of 7500 mg/kg in sediments (Duruibe *et al.*, 2007). The exceeded limits for Zn in prawns and water is up to 1.7 and 5 – 7.0 folds respectively. The concentration of the Zn and Pb also exceed that of Rumisha *et al.* (2017). The acceptable limits of heavy metals in sediments are 85 mg/kg for Cd, 1 mg/kg for Hg, and 420 mg/kg for Pb respectively (Choi, 2011; Arulkumar, 2017). Therefore, concentration of Cd, Hg and Zn in sediments was below the acceptable limits.

The limit for Pb in prawns is 0.30 mg/kg Arulkumar (2017) and 0.5 mg/kg FAO (1983) and for water is 0.0058 mg/L (Duruibe *et al.*, 2007). Therefore, prawns contained 80 - 83 folds higher concentration of Pb and 3 - 208 folds in water respectively. Higher accumulation of Pb in marine prawns and water was also reported in other studies (Abdenmour *et al.*, 2000; Förstner & Wittmann, 2012). In contrast, Pb concentration in sediments was found to be below acceptable limits of 420 mg/kg.

Furthermore, Cd concentrations in all samples of prawns, sediments and water analyzed were above the European Union EU (2001) limit of 0.05 mg/kg; United States Environmental Protection Agency [USEPA] (2000) and EUROPA (2004) limit of 0.10 mg/kg, respectively. Ali *et al.* (2016) reported that, anthropogenic activities can effortlessly generate heavy metals in sediments and water that pollute the aquatic environment. Conversely, Cd concentration in water was below the limit set by the Malaysian Food Regulation (1985) i.e., 1.0 mg/kg. According to Hong Kong Environmental Protection Department [HKEPD] (1987) the recommended limit is 2.0 mg/kg by United States Food and Drug Administration USFDA. (1993) is 3.70 mg/kg of which the levels reported in this study were within the acceptable limits. Additionally, Hg detected were all below the acceptable limits in sediments and water; and 0.38 folds higher in prawns from Kisiju.

The anthropogenic activities around the coastal area and discharge of oil from cargo ships pollutes water, especially at Bagamoyo as a result of high concentrations of heavy metals (Khalifa *et al.*, 2010). Heavy metals cannot be destroyed or degraded and can enter in human bodies through food chain including prawns, water and air inhalation. Heavy metals have ability to accumulate in marine environmental Lundy *et al.* (2017) and marine organisms such as prawns. If the concentration exceeds the acceptable levels, it becomes toxic to prawns and may cause health problems to prawns as reported by Mmochi and Francis (2003) as well as posing health risks to human.

Short and long term exposure to Pb can cause brain damage, paralysis, gastrointestinal symptoms. Zinc, Pb and *lambda*-cyhalothrin contaminants indicate a potential safety risk of prawn consumers and marine environment. If large doses of zinc are taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting may occur as zinc influences apoptosis by acting on several molecular regulators of programmed cell death (Plum *et al.*, 2010). Ingesting high level of heavy metal, damage to the kidneys, reproductive and immune systems as well as effects on the nervous system Yedjou *et al.* (2010) levels of zinc for several

months may cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) (Plum *et al.*, 2010). Also, the effect of *lambda*-cyhalothrin in human including damage to the lungs, nervous, birth defects and even cancer also dizziness, headache, nausea, lack of appetite, and fatigue and in severe poisonings, seizures and coma may occur (Basir *et al.*, 2011).

Table 15: Heavy metals concentration in the study zones

Zones	Concentration (Mean \pm SD)			
	Pb	Zn	Cd	Hg
Bagamoyo				
Prawns	24.29 \pm 1.73 ^a	107.16 \pm 2.65 ^c	1.04 \pm 0.07 ^a	0.07 \pm 0.03 ^a
Sediments	31.66 \pm 3.43 ^a	152.50 \pm 20.80 ^a	1.80 \pm 0.13 ^a	0.05 \pm 0.01 ^a
Water	1.21 \pm 0.46 ^a	0.64 \pm 0.11 ^a	0.15 \pm 0.03 ^a	0.03 \pm 0.01 ^a
Kilwa				
Prawns	24.91 \pm 1.43 ^a	166.06 \pm 7.14 ^a	1.17 \pm 0.03 ^a	0.05 \pm 0.01 ^a
Sediments	35.07 \pm 10.54 ^a	133.44 \pm 35.98 ^a	1.50 \pm 0.24 ^b	0.04 \pm 0.01 ^a
Water	0.43 \pm 0.07 ^b	0.39 \pm 0.22 ^b	0.04 \pm 0.0 ^b	0.03 \pm 0.01 ^a
Kisiju				
Prawns	24.75 \pm 1.59 ^a	153.89 \pm 0.61 ^c	0.18 \pm 0.05 ^a	0.19 \pm 0.24 ^b
Sediments	28.13 \pm 3.44 ^a	153.49 \pm 9.35 ^a	1.63 \pm 0.08 ^{ab}	0.05 \pm 0.01 ^a
Water	0.02 \pm 0.61 ^c	0.49 \pm 0.20 ^{ab}	0.02 \pm 0.11 ^b	0.03 \pm 0.01 ^a

Note: Mean concentrations for prawns and sediments (mg/kg), and water (mg/L). Mean \pm SD, (n=3), Means with different superscripts on the same group across the column are significant at $p < 0.05$.

The maximum acceptable limit for sediments; Zn: 7500 mg/kg, Pb: 420 mg/kg, Cd: 85mg/kg and Hg 1mg/kg. Prawns; Zn: 100 mg/kg, Pb: 0.3mg/kg, Cd: 2 mg/kg and Hg 0.5 mg/kg. Water; Zn: 0.0766 mg/L, Pb: 0.0058 mg/l, Cd: 0.008 mg/L and Hg 0.05 mg/L. Limit of detection was Zn: 0.01 mg/kg, Pb: 0.01 mg/kg, Cd: 0.001 mg/kg and Hg: 0.001 mg/kg.

The maximum acceptable limits of heavy metals in prawns are Zn 100 mg/kg, Pb 0.3 mg/kg, Cd, 2 mg/kg and for Hg 0.5 mg/kg (Choi, 2011; Arulkumar, 2017). From the above results Zn and Pb in prawns are above acceptable limit in all of the three zones of Bagamoyo, Kilwa and Kisiju. The Maximum acceptable limits of heavy metals in sediments are 7500 Zn, 85 mg/ for Cd, 0.008 mg/kg for Hg, and 420 mg/kg for Pb (Choi, 2011; Arulkumar, 2017). From the above results all heavy metals are within the acceptable level in sediments in all of the three zones of Bagamoyo, Kilwa and Kisiju. The Maximum acceptable limits of heavy metals in water are Zn 0.0766 mg/L, Pb 0.0588 mg/L, Cd, 2 mg/L and for Hg 0.05 mg/L (Choi, 2011; Arulkumar, 2017). From the above results Pb in water are above acceptable limit in Kilwa and Bagamoyo zones and Zn, Cd and Hg are within the acceptable level.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The study concludes that, prawns in the study areas were found to be contaminated with heavy metals (Pb and Zn) and *lambda*-cyhalothrin at levels beyond the acceptable levels. This calls for immediate and frequent monitoring of anthropogenic activities around the nursery areas for prawns so as to safeguard the public health and ecosystem. In addition, a comprehensive risk assessment is needed to shade more light on the status quo of heavy metals and pesticide residues to the human population in the areas. Moreover, the findings from this study can serve as a baseline information for future monitoring and risk assessment studies.

5.2 Recommendations

- (i) Assessing and/or monitoring of the pesticides at the supplier point before they are distributed to farmers. This will ensure that active ingredient(s) written outside the container are in the product concern (authenticity of the pesticides).
- (ii) Also monitoring of fishing activities around the delta should be done regularly so as to control the agricultural activities around the area.
- (iii) Risk assessment should be done to evaluate Zn, Pb and *lambda*-cyhalothrin exposure to prawns consumers.
- (iv) Training on sustainable prawn's fishing/management to the fishing zones is necessary to raise awareness on how to minimize potential risks to marine pollution.
- (v) Further study should be done on characterization of sediments sample around the study area to in order to know the impact of the sediments around the study area.
- (vi) Further study should be done on the seasonality effect on the heavy metals and pesticide residues around the study site Bagamoyo, Kilwa and Kisiju zone.

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APPENDICES

Appendix 1: Questionnaire

THE NELSON MANDELA AFRICAN INSTITUTION OF SCIENCE AND TECHNOLOGY



SCHOOL OF LIFE SCIENCE AND BIOENGINEERING

DEPARTMENT OF FOOD BIOTECHNOLOGY AND NUTRITIONAL SCIENCES

PROGRAMME: MASTERS OF FOOD AND NUTRITIONAL SCIENCES

Questionnaire for follow up survey for the Research titled: Marine Pollutants as Quality Determinant For Sustainable Management of Prawns Along the Indian Coastline of Tanzania

I. Interviewer information

Name of an interviewer..... Date/...../.....

II. Respondent information

A. Demographic information

1. Name of the respondent..... Code.....
2. Sex Male ☐ Female ☐
3. Marital status : Single ☐ Married ☐ Divorced ☐ Widowed ☐
4. Date of birth/...../..... 1`
5. Education level : None ☐ primary school ☐ secondary school ☐ Higher ☐
6. Occupation: Farmer ☐ Employee ☐ Businessman ☐ Student ☐ None ☐
7. Family size
8. Religion a) Christian b) Muslim c) others..... ☐
9. Where do you live?
 - a) Region.....
 - b) District.....
 - c) Ward.....
 - d) Village/street..... ☐

B. Fishing activities

10. What kind of fish available in this area. (put √ for appropriate answer)
 - a) Prawns
 - b) Tuna
 - c) King fish
 - d) Others (specify)
11. Quantity of it per day
 - a) Below 10kg
 - b) Below 50kg

- c) Below 100kg
- 12. How many times do they fish per day?
 - a) 1
 - b) 2
 - c) More than 2
- 13. What kind of fishing gears used?
 - a) Gill net
 - b) Scoop net
 - c) Others(specify)
- 14. In which area are they fishing
 - a) Open space
 - b) Blackish water
 - c) Others (specify)
- 15. As compared to previous years the catch has increased or decreased if yes for what kg and if no for what kg per day
 - a) Below 10
 - b) Below 50
 - c) Below 100
- 16. How many fisherman are fishing per day
 - a) Below 10
 - b) Below 50
 - c) Below 100

B: Agricultural practice, industrial and illegal fishing.

- 17. Is there any agricultural practice going on around the area?
 - a) No
 - b) Sometimes
 - c) Usually
- 18. Which kind of scale of agricultural practice going on
 - a) large
 - b) medium
 - c) small
- 19. Is there any industrial activities going on in this area
 - a) Yes
 - b) No
 - c) I don't know
- 20. Frequent of industrial practice going on in the area?
 - a) Everyday
 - b) 1-2
 - c) 3-5
 - d) None
- 21. Do you practice agriculture
 - a)Yes
 - b) No

- 22. What size of farm do you have hectare
 - a) 1
 - b) 2
 - c) 3
 - d)4

23. What kind of crops grown in this area
- a) Rice
 - b) Maize
 - c) Cassava
 - d) Tomatoes
 - e) Cashnuts
 - f) Coconut
 - g) Vegetable
 - h) Not applicable
24. What type of pesticide used in this farm?
- a) DDT
 - b) *Karatii*
 - c) Ninja
 - d) *Rungu*
 - e) Cyberdip
 - f) Commander
 - g) Nil
25. What type of herbicide used in this area?
- a) Roundup
 - b) Commander
 - c) Weedall
 - d) Herbicide
 - e) Nil
26. What type of fertilizer used?
- a) UREA
 - b) NPK
 - c) Buster
 - d) Nil
27. Are there any case of using poison for fishing?
- a) Below 10
 - b) Below 20
 - c) None
28. Are there any case of using dynamite for fishing?
- a) Everyday
 - b) 1-2
 - c) 3-5
 - d) None

C. Fish Quality loss

29. Is there any loss due to quality deterioration? Yes or No
- a) Every day
 - b) 3 – 5

- c) None
- 30. How many times did the loss occur.
 - a) Every day
 - b) 3 – 5
 - c) None (specify)
- 23 . How many fishermen are dealing with prawns fishing
 - a) Below 10
 - b) Below 50
 - c) Below 100
 - d) None (specify)
- 31. What size of gill net are used for prawns fishing.
 - a) 3mm
 - b) 2mm
 - c) 1mm
 - d) None (specify).
- 32. What kind of species by-catch found after fishing.
 - a) Small sardine
 - b) Shrimp
 - c) King fish
 - d) Others (specify)

Appendix 2: Statistical Analysis for Questionnaires Data

```
FREQUENCIES VARIABLES=Gender Mar.stat Age_group Lev.edu Occupation Head.House Number.in.house Religion Zone Type.fish Presence_prawn
_fished Kg_prawns Freq.prawns Fish_gears Loc_fishing Stat_yield Amount_declined Number_of_Fsh Rumouis_pois_fis If_yes_type_pos Number
ses_pos Rumous_dynamite Freq_week_dyn Wastes_det If_howmuch N_prawn_fisherman Size_gilnet By_Capture Agri_activities Size_agr Type_cr
Size_farm Pesticide_used Herbicide Fertilizer Industrial_act Freq_industr_act
/ORDER=ANALYSIS.
```

→ Frequencies

[DataSet1] C:\Users\Hp\Desktop\Qustionnaire_data.sav

		Gender of the Interviewee	Marital Status	Age group of the interviewee	Level of education	Occupation of the interviewee	Are you head of the household?	Number of people in the house	Religion type	Zone of the interviewee	Type of the fish
N	Valid	122	122	0	122	122	122	122	122	122	122
	Missing	0	0	122	0	0	0	0	0	0	0

Frequency Table

Gender of the Interviewee

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Man	102	83.6	83.6	83.6
	Woman	20	16.4	16.4	100.0
	Total	122	100.0	100.0	

Marital Status

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Un-married	10	8.2	8.2	8.2
	Married	96	78.7	78.7	86.9
	Separated	12	9.8	9.8	96.7
	Divorsed	2	1.6	1.6	98.4
	Widow	1	.8	.8	99.2
	Leave without married	1	.8	.8	100.0
	Total	122	100.0	100.0	

Age group of the interviewee

		Frequency	Percent
Missing	System	122	100.0

Level of education

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Uneducated	17	13.9	13.9	13.9
	Primary	90	73.8	73.8	87.7
	Secondary	15	12.3	12.3	100.0
	Total	122	100.0	100.0	

Occupation of the interviewee					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Fisherman	64	52.5	52.5	52.5
	Peasant	44	36.1	36.1	88.5
	Businessman	12	9.8	9.8	98.4
	Others	2	1.6	1.6	100.0
	Total	122	100.0	100.0	

Are you head of the household?					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Yes	101	82.8	82.8	82.8
	No	21	17.2	17.2	100.0
	Total	122	100.0	100.0	

Number of people in the house					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	<3	18	14.8	14.8	14.8
	3-5	45	36.9	36.9	51.6
	>=6	57	46.7	46.7	98.4
	Not applicable	2	1.6	1.6	100.0
	Total	122	100.0	100.0	

Zone of the interviewee					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Bagamoyo	39	32.0	32.0	32.0
	Kilwa	41	33.6	33.6	65.6
	Kisiju	39	32.0	32.0	97.5
	Other's	3	2.5	2.5	100.0
	Total	122	100.0	100.0	

Type of the fish					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Changu	7	5.7	5.7	5.7
	Kolekole	8	6.6	6.6	12.3
	Koano	4	3.3	3.3	15.6
	Dagaa kamba	6	4.9	4.9	20.5
	Dagaa Mchele	10	8.2	8.2	28.7
	Kibua	18	14.8	14.8	43.4
	Ndevu	3	2.5	2.5	45.9
	Kipuapua	3	2.5	2.5	48.4
	Hongwe	10	8.2	8.2	56.6
	Msusa	4	3.3	3.3	59.8
	Mbalata	26	21.3	21.3	81.1
	Chewa	7	5.7	5.7	86.9
	Mboke	15	12.3	12.3	99.2
	Tilapia	1	.8	.8	100.0
	Total	122	100.0	100.0	

Amount of fish yield per day				
	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <10	44	36.1	36.1	36.1
<30	15	12.3	12.3	48.4
<50	27	22.1	22.1	70.5
>50	36	29.5	29.5	100.0
Total	122	100.0	100.0	

Amount of prawns yield per day				
	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <10	38	31.1	31.1	31.1
<30	29	23.8	23.8	54.9
<50	36	29.5	29.5	84.4
>50	19	15.6	15.6	100.0
Total	122	100.0	100.0	

Frequency per day of fishing prawns					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid Once	84	68.9	68.9	68.9	
Twice	32	26.2	26.2	95.1	
Above twice	6	4.9	4.9	100.0	
Total	122	100.0	100.0		

Type of fishing gears used for fishing					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid Gillnet	96	78.7	78.7	78.7	
Ring net	18	14.8	14.8	93.4	
Pin	8	6.6	6.6	100.0	
Total	122	100.0	100.0		

Location of the fishing					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid River	22	18.0	18.0	18.0	
Eustaries	2	1.6	1.6	19.7	
Mangroove	42	34.4	34.4	54.1	
Deep sea	12	9.8	9.8	63.9	
Shallow sea	19	15.6	15.6	79.5	
All	16	13.1	13.1	92.6	
Mwamba	9	7.4	7.4	100.0	
Total	122	100.0	100.0		

Is the status of fish yield declined or raised					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid Declained	94	77.0	77.0	77.0	
Raised	17	13.9	13.9	91.0	
Same	11	9.0	9.0	100.0	
Total	122	100.0	100.0		

How much is the decline

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <10	22	18.0	18.0	18.0
<30	4	3.3	3.3	21.3
<50	19	15.6	15.6	36.9
>50	51	41.8	41.8	78.7
Not applicable	26	21.3	21.3	100.0
Total	122	100.0	100.0	

How many fisherman are fishing per day

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <10	9	7.4	7.8	7.8
<30	22	18.0	19.0	26.7
<50	36	29.5	31.0	57.8
>50	29	23.8	25.0	82.8
Nil	20	16.4	17.2	100.0
Total	116	95.1	100.0	
Missing System	6	4.9		
Total	122	100.0		

Is there any roumerous on fishing using poisons

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid Yes	25	20.5	20.5	20.5
No	97	79.5	79.5	100.0
Total	122	100.0	100.0	

If yes what type of poisoning used

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid Utupa	8	6.6	6.6	6.6
Cybedip	9	7.4	7.4	13.9
Not applicable	96	78.7	78.7	92.6
I do'nt know	6	4.9	4.9	97.5
chupa za gesi ya oxygen	2	1.6	1.6	99.2
Dawa ya kupulizia maiti	1	.8	.8	100.0
Total	122	100.0	100.0	

Number of fisherman using poisoning

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <5	10	8.2	8.2	8.2
<10	9	7.4	7.4	15.6
>10	2	1.6	1.6	17.2
Not applicable	101	82.8	82.8	100.0
Total	122	100.0	100.0	

Is there any roumerous on fishing using dynamite poisons

	Frequency	Percent	Valid Percent	Cumulative Percent
Valid Yes	23	18.9	18.9	18.9
No	99	81.1	81.1	100.0
Total	122	100.0	100.0	

Frequency per week on dynamite fishing

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Everyday	5	4.1	4.1	4.1
	1-2	14	11.5	11.5	15.6
	3-5	5	4.1	4.1	19.7
	Not applicable	98	80.3	80.3	100.0
	Total	122	100.0	100.0	

Is there any fish wastes due to rotting

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Yes	1	.8	.8	.8
	No	121	99.2	99.2	100.0
	Total	122	100.0	100.0	

If Yes how much per day?

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	<10	1	.8	.8	.8
	Not applicable	121	99.2	99.2	100.0
	Total	122	100.0	100.0	

Number of fisher man fishing prawns

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	<10	25	20.5	20.5	20.5
	<30	27	22.1	22.1	42.6
	<50	47	38.5	38.5	81.1
	>50	11	9.0	9.0	90.2
	I dont know	12	9.8	9.8	100.0
	Total	122	100.0	100.0	

Size of the net used for fishing (Inches)

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	1	14	11.5	11.5	11.5
	2	67	54.9	54.9	66.4
	3	6	4.9	4.9	71.3
	I dont know	35	28.7	28.7	100.0
	Total	122	100.0	100.0	

What kind of species by-catch found after fishing.

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Mbalata	37	30.3	30.3	30.3
	Dagaa	17	13.9	13.9	44.3
	Kolekole	11	9.0	9.0	53.3
	Mbulambula	1	.8	.8	54.1
	Bumbula	5	4.1	4.1	58.2
	Chaa	4	3.3	3.3	61.5
	Not applicable	5	4.1	4.1	65.6
	I dont know	9	7.4	7.4	73.0
	Kipuapua	5	4.1	4.1	77.0
	Msusa	6	4.9	4.9	82.0
	Shembea	2	1.6	1.6	83.6
	Mboke	8	6.6	6.6	90.2
	chewa	4	3.3	3.3	93.4
	Msembwe	4	3.3	3.3	96.7
	Vibua	1	.8	.8	97.5
	Chongole	3	2.5	2.5	100.0
	Total	122	100.0	100.0	

Is there any agricultural activities

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Yes	97	79.5	79.5	79.5
	No	21	17.2	17.2	96.7
	Idont know	4	3.3	3.3	100.0
	Total	122	100.0	100.0	

What size of the agricultural activities

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Small	37	30.3	30.3	30.3
	Medium	46	37.7	37.7	68.0
	Large	13	10.7	10.7	78.7
	Not applicable	26	21.3	21.3	100.0
	Total	122	100.0	100.0	

Type of the crop harvested

		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	Rice	79	64.8	64.8	64.8
	Maize	8	6.6	6.6	71.3
	Cassava	5	4.1	4.1	75.4
	Tomatoes	2	1.6	1.6	77.0
	Cashewnut	1	.8	.8	77.9
	Vegetables	1	.8	.8	78.7
	Not applicable	26	21.3	21.3	100.0
	Total	122	100.0	100.0	

Size of farm in acers				
	Frequency	Percent	Valid Percent	Cumulative Percent
Valid <1	4	3.3	3.3	3.3
<2	33	27.0	27.0	30.3
<3	37	30.3	30.3	60.7
>3	10	8.2	8.2	68.9
Nil	38	31.1	31.1	100.0
Total	122	100.0	100.0	

Type of the pesticides used					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid DDT	7	5.7	5.7	5.7	
Karatii	31	25.4	25.4	31.1	
Ninja	20	16.4	16.4	47.5	
Rungu	3	2.5	2.5	50.0	
Cybadip	7	5.7	5.7	55.7	
Commander	5	4.1	4.1	59.8	
Nil	49	40.2	40.2	100.0	
Total	122	100.0	100.0		

What is the frequency of industrial activities per week					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid Once	1	.8	.8	.8	
3-5	9	7.4	7.4	8.2	
Not applicable	112	91.8	91.8	100.0	
Total	122	100.0	100.0		

Type of herbicide					
	Frequency	Percent	Valid Percent	Cumulative Percent	
Valid Roundup	41	33.6	33.6	33.6	
Commander	8	6.6	6.6	40.2	
Weedall	15	12.3	12.3	52.5	
Herbicide	10	8.2	8.2	60.7	
Nil	48	39.3	39.3	100.0	
Total	122	100.0	100.0		

Type of fertilizer				
	Frequency	Percent	Valid Percent	Cumulative Percent
Valid UREA	38	31.1	31.1	31.1
NPK	10	8.2	8.2	39.3
Boster	26	21.3	21.3	60.7
Nil	48	39.3	39.3	100.0
Total	122	100.0	100.0	

Is there any industrial activities?				
	Frequency	Percent	Valid Percent	Cumulative Percent
Valid Yes	9	7.4	7.4	7.4
No	104	85.2	85.2	92.6
I dont know	9	7.4	7.4	100.0
Total	122	100.0	100.0	

Appendix 3: Statistical results for pesticide residue *Lambda*-cyhalothrin

Name	Type	Value
Glory_pesticides_lm	list [13] (S3: lm)	List of length 13
coefficients	double [3]	0.648 11.559 15.846
residuals	double [6]	-0.583 0.583 -2.293 2.293 -1.671 1.671
effects	double [6]	-23.963 4.199 15.846 2.955 -2.780 0.563
rank	integer [1]	3
fitted.values	double [6]	0.648 0.648 12.207 12.207 16.494 16.494
assign	integer [3]	0 1 1
qr	list [5] (S3: qr)	List of length 5
df.residual	integer [1]	3
contrasts	list [1]	List of length 1
xlevels	list [1]	List of length 1
call	language	lm(formula = Lamda_cyhalothrin ~ Zones)
terms	formula	Lamda_cyhalothrin ~ Zones
model	list [6 x 2] (S3: data.frame)	A data.frame with 6 rows and 2 columns

Results *Lambda*-cyhalothrin for sediments

	Zones	Response
1	Bagamoyo	0.06481833
2	Bagamoyo	1.23094696
3	Kilwa	9.91445120
4	Kilwa	14.49968350
5	Kisiju	14.82285732
6	Kisiju	18.16549563

Results: *Lambda*-cyhalothrin for sediments

Name	Type	Value
PesticidesHSD	list [5] (S3: group)	List of length 5
statistics	list [1 x 5] (S3: data.frame)	A data.frame with 1 rows and 5 columns
parameters	list [1 x 5] (S3: data.frame)	A data.frame with 1 rows and 5 columns
means	list [3 x 8] (S3: data.frame)	A data.frame with 3 rows and 8 columns
comparison	NULL	Pairlist of length 0
groups	list [3 x 2] (S3: data.frame)	A data.frame with 3 rows and 2 columns

Statistical results for pesticide residue *Lambda*-cyhalothrin (Sediments)

Analysis of Variance Table

Response: Lamda_cyhalothrin

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Zones	2	268.733	134.366	24.024	0.01425 *
Residuals	3	16.779	5.593		

signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

> |

Statistical results for pesticide residue *Lambda*-cyhalothrin (Prawns)

Analysis of Variance Table

Response: Lamda_cyhalothrin

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Zones	2	268.733	134.366	24.024	0.01425 *
Residuals	3	16.779	5.593		

signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

> |

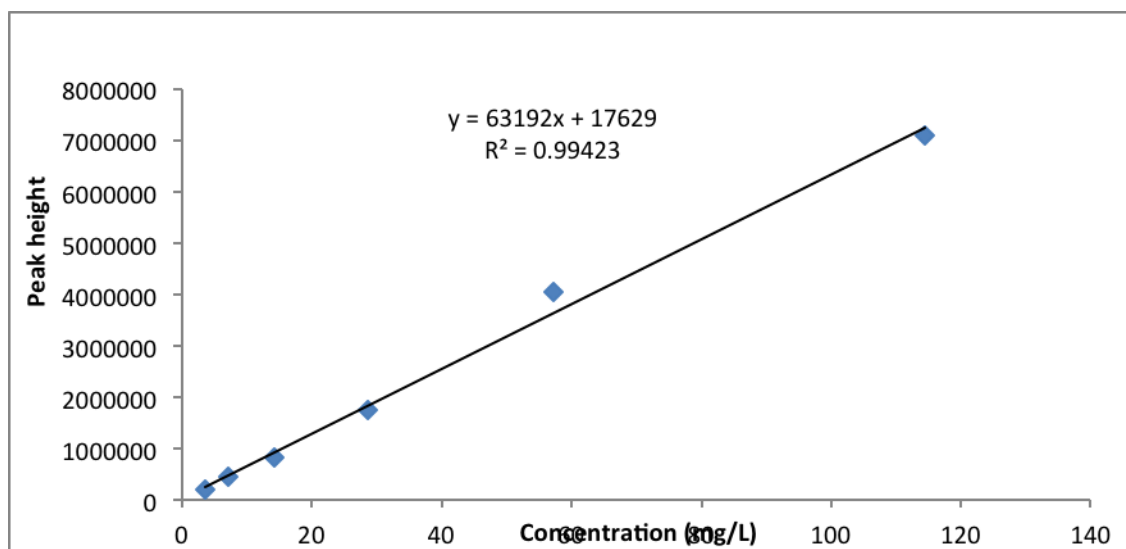
Statistical results for prawns

Filter		
	Zones	Response
1	Bagamoyo	0.0000000
2	Bagamoyo	0.0000000
3	Kilwa	0.0000000
4	Kilwa	0.5639005
5	Kisiju	1.8983732
6	Kisiju	2.6289720

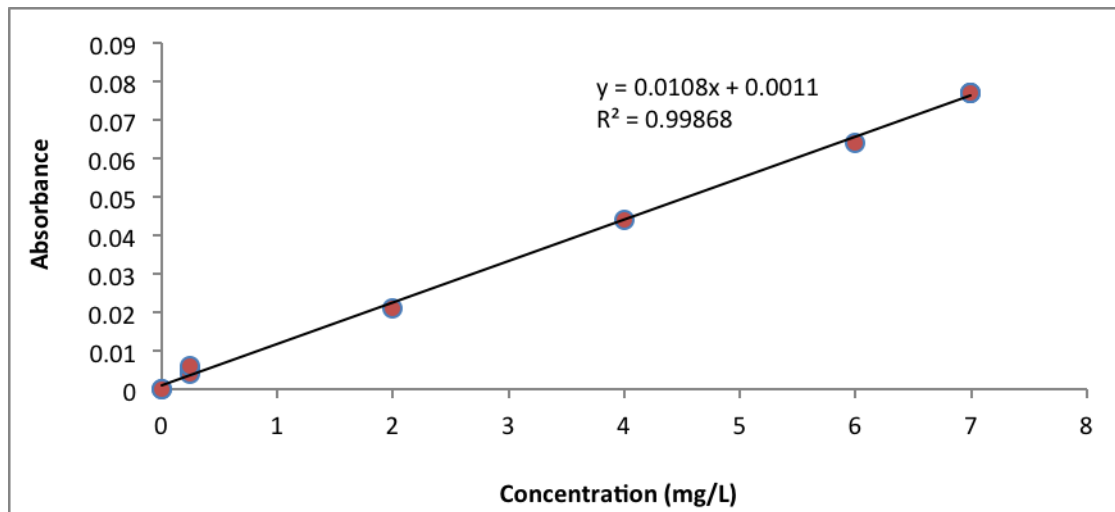
Name	Type	Value
▼ PesticidesHSD	list [5] (S3: group)	List of length 5
▶ statistics	list [1 x 5] (S3: data.frame)	A data.frame with 1 rows and 5 columns
▶ parameters	list [1 x 5] (S3: data.frame)	A data.frame with 1 rows and 5 columns
▶ means	list [3 x 8] (S3: data.frame)	A data.frame with 3 rows and 8 columns
comparison	NULL	Pairlist of length 0
▶ groups	list [3 x 2] (S3: data.frame)	A data.frame with 3 rows and 2 columns

Appendix 4: Standard calibration curve

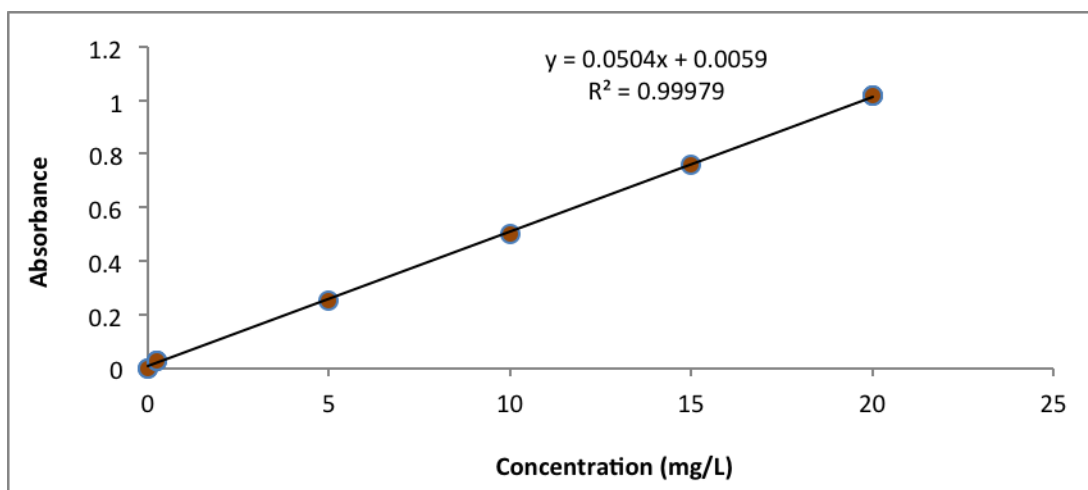
Pl9 pesticide residue (Lambda-cyhalothrin)



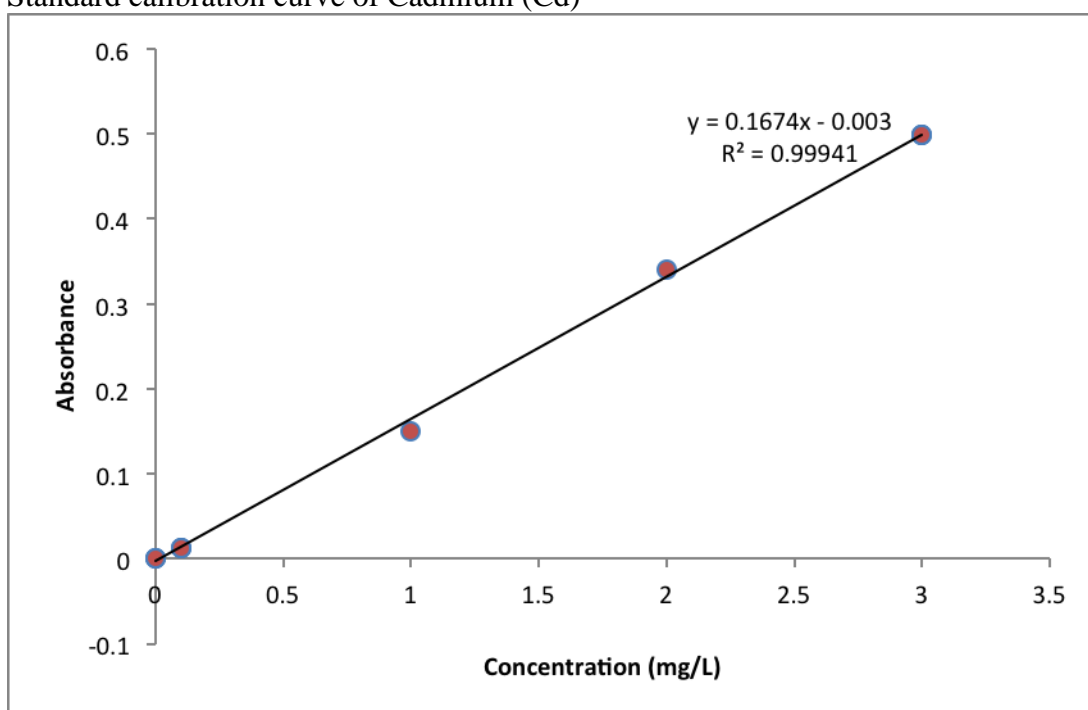
Standard calibration curve of Lead (Pb)



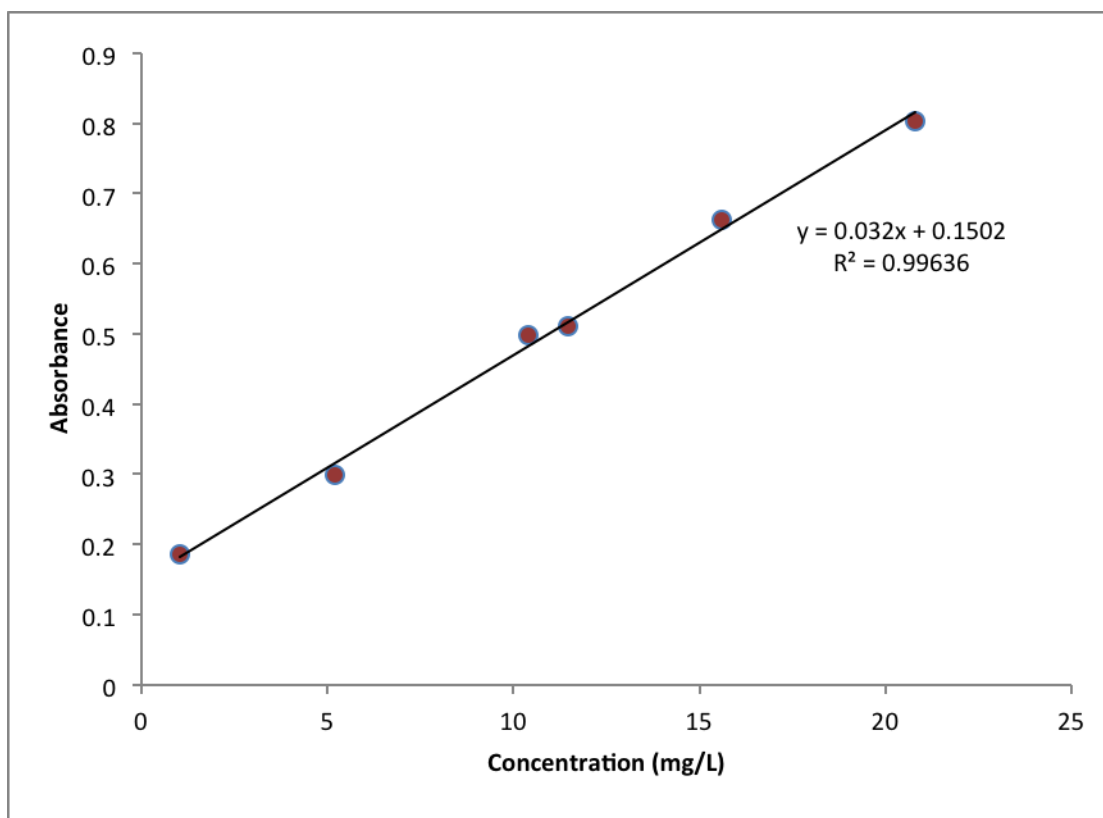
Standard calibration curve of Zinc (Zn)



Standard calibration curve of Cadmium (Cd)



Standard calibration curve of Mercury (**Hg**)



Appendix 5: R-codes for heavy metals

```
heavy metal R codes - Notepad
File Edit Format View Help
library(readxl)
heavy_metals <- read_excel("C:/Users/Hp/Desktop/heavy_metals.xlsx",
                           sheet = "Water")

#.....WATER.....
water=heavy_metals
attributes(water)
|
#.....Pb.....
lmwater=lm(water$Pb_conc~water$Zone)
aovwaterpb=aov(lmwater)
aovwaterpb
anova(lmwater)
library(agricolae)
waterpb.Tukey=TukeyHSD(aovwaterpb,"water$Zone")
print(waterpb.Tukey)
waterpbHSD=HSD.test(aovwaterpb,"water$Zone", group=TRUE)
print(waterpbHSD)

#.....Zn.....
lmwaterzn=lm(water$Zn_conc~water$Zone)
aovwaterzn=aov(lmwaterzn)
aovwaterzn
anova(lmwaterzn)
waterzn.Tukey=TukeyHSD(aovwaterzn,"water$Zone")
print(waterzn.Tukey)
waterznHSD=HSD.test(aovwaterzn,"water$Zone", group=TRUE)
print(waterznHSD)

#.....Cd.....
lmwatercd=lm(water$Cd_conc~water$Zone)
aovwatercd=aov(lmwatercd)
aovwatercd
anova(lmwatercd)
watercd.Tukey=TukeyHSD(aovwatercd,"water$Zone")
print(watercd.Tukey)
watercdHSD=HSD.test(aovwatercd,"water$Zone", group=TRUE)
print(watercdHSD)
```



```
#.....Hg.....
lmwaterhg=lm(water$Hg_conc~water$Zone)
aovwaterhg=aov(lmwaterhg)
aovwaterhg
anova(lmwaterhg)
waterhg.Tukey=TukeyHSD(aovwaterhg,"water$Zone")
print(waterhg.Tukey)
waterhgHSD=HSD.test(aovwaterhg,"water$Zone", group=TRUE)
print(waterhgHSD)

#.....PRAWNS.....
library(readxl)
heavy_metals <- read_excel("C:/Users/Hp/Desktop/heavy_metals.xlsx",
                           sheet = "Prawns")

prawns=heavy_metals
attributes(prawns)

#.....Pb.....
lmprawns=lm(prawns$Pb_conc~prawns$Zone)
aovprawns=lmprawns
aovprawns
anova(lmprawns)
library(agricolae)
prawns.Tukey=TukeyHSD(aovprawns,"prawns$Zone")
print(prawns.Tukey)
prawnsHSD=HSD.test(aovprawns,"prawns$Zone", group=TRUE)
print(prawnsHSD)

#.....Zn.....
lmprawnszn=lm(prawns$Zn_conc~prawns$Zone)
aovprawnszn=aov(lmprawnszn)
aovprawnszn
anova(lmprawnszn)
prawnszn.Tukey=TukeyHSD(aovprawnszn,"prawns$Zone")
print(prawnszn.Tukey)
prawnsznHSD=HSD.test(aovprawnszn,"prawns$Zone", group=TRUE)
print(prawnsznHSD)
```

```
#.....Cd.....
lmprawnsd=lm(prawns$Cd_conc~prawns$Zone)
aovprawnsd=aov(lmprawnsd)
aovprawnsd
anova(lmprawnsd)
prawnsd.Tukey=TukeyHSD(aovprawnsd,"prawns$Zone")
print(prawnsd.Tukey)
prawnsdHSD=HSD.test(aovprawnsd,"prawns$Zone", group=TRUE)
print(prawnsdHSD)
#.....Hg.....
lmprawnshg=lm(prawns$Hg_conc~prawns$Zone)
aovprawnshg=aov(lmprawnshg)
aovprawnshg
anova(lmprawnshg)
prawnshg.Tukey=TukeyHSD(aovprawnshg,"prawns$Zone")
print(prawnshg.Tukey)
prawnshgHSD=HSD.test(aovprawnshg,"prawns$Zone", group=TRUE)
print(prawnshgHSD)

#.....SEDIMENTS.....
library(readxl)
heavy_metals <- read_excel("C:/Users/Hp/Desktop/heavy_metals.xlsx",
                           sheet = "Sediment")
sediment=heavy_metals
attributes(sediment)

#.....Pb.....
lmsediment=lm(sediment$Pb_conc~sediment$Zone)
aovsedimentpb=aov(lmsediment)
aovprawnsdpb
anova(lmsediment)
library(agricolae)
sedimentpb.Tukey=TukeyHSD(aovsedimentpb,"sediment$Zone")
print(sedimentpb.Tukey)
```

```
aovsedmentpb=aov(lmsedment)
aovprawnsnpb
anova(lmsedment)
library(agricolae)
sedmentpb.Tukey=TukeyHSD(aovsedmentpb,"sedment$Zone")
print(sedmentpb.Tukey)
sedmentpbHSD=HSD.test(aovsedmentpb,"sedment$Zone", group=TRUE)
print(sedmentpbHSD)
#.....Zn.....
lmsedmentzn=lm(sedment$Zn_conc~sedment$Zone)
aovsedmentzn=aov(lmsedmentzn)
aovsedmentzn
anova(lmprawnszn)
sedmentzn.Tukey=TukeyHSD(aovsedmentzn,"sedment$Zone")
print(sedmentzn.Tukey)
sedmentznHSD=HSD.test(aovsedmentzn,"sedment$Zone", group=TRUE)
print(sedmentznHSD)

#.....Cd.....
lmsedmentcd=lm(sedment$Cd_conc~sedment$Zone)
aovsedmentcd=aov(lmsedmentcd)
aovsedmentcd
anova(lmsedmentcd)
sedmentcd.Tukey=TukeyHSD(aovsedmentcd,"sedment$Zone")
print(sedmentcd.Tukey)
sedmentcdHSD=HSD.test(aovsedmentcd,"sedment$Zone", group=TRUE)
print(sedmentcdHSD)
#.....Hg.....
lmsedmenthg=lm(sedment$Hg_conc~sedment$Zone)
aovsedmenthg=aov(lmsedmenthg)
aovsedmenthg
anova(lmsedmenthg)
sedmenthg.Tukey=TukeyHSD(aovsedmenthg,"sedment$Zone")
print(sedmenthg.Tukey)
sedmenthgHSD=HSD.test(aovsedmenthg,"sedment$Zone", group=TRUE)
print(sedmenthgHSD)
```

R-codes for Pesticide residue

R.Code_pesticides - Notepad

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```
library(ggplot2)
#.....Calibration curve.....
concentration_mg_kg=c(114.5,57.25,28.625,14.3125,7.15625,3.578125)
pheight=c(7085435,4037650,1756394,812776,454588,203903)
re_glory=lm(pheight~concentration_mg_kg)
plot(pheight~concentration_mg_kg,main="Calibration curve of lamda cyhalothrin",
      xlab="Concentration (mg/kg)",ylab="Peak height")
abline(re_glory)
summary(re_glory)
#.....test for indepenence
[ #.....ANOVA Sediment data analysis.....
Zones=c(rep("Bagamoyo",2),rep("Kilwa",2),rep("Kisiju",2))
Zones=factor(Zones)
Lamda_cyhalothrin=c(0.064818331,1.230946955,9.914451196,14.4996835,14.82285732,18.16549563)
Glory_pesticides=data.frame(Zones=factor(Zones),Response=Lamda_cyhalothrin)
summary(Glory_pesticides)
Glory_pesticides_lm=lm(Lamda_cyhalothrin~Zones)
ANOVAPEST=anova(Glory_pesticides_lm)
print(ANOVAPEST)
#.....Testing for means significance (mean separation) Zones in sediments.....

Cyhalothrin_aov=aov(Lamda_cyhalothrin~Zones)
library(agricolae)
Cyhalothrin.Tukey=TukeyHSD(Cyhalothrin_aov,"Zones")
print(Cyhalothrin.Tukey)
plot(Cyhalothrin.Tukey)
PesticidesHSD=HSD.test(Cyhalothrin_aov, "Zones", group=TRUE)
print(PesticidesHSD)
```

R.Code_pesticides - Notepad

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```
#.....test for indepenence
[ #.....ANOVA Sediment data analysis.....
Zones=c(rep("Bagamoyo",2),rep("Kilwa",2),rep("Kisiju",2))
Zones=factor(Zones)
Lamda_cyhalothrin=c(0.064818331,1.230946955,9.914451196,14.4996835,14.82285732,18.16549563)
Glory_pesticides=data.frame(Zones=factor(Zones),Response=Lamda_cyhalothrin)
summary(Glory_pesticides)
Glory_pesticides_lm=lm(Lamda_cyhalothrin~Zones)
ANOVAPEST=anova(Glory_pesticides_lm)
print(ANOVAPEST)
#.....Testing for means significance (mean separation) Zones in sediments.....

Cyhalothrin_aov=aov(Lamda_cyhalothrin~Zones)
library(agricolae)
Cyhalothrin.Tukey=TukeyHSD(Cyhalothrin_aov,"Zones")
print(Cyhalothrin.Tukey)
plot(Cyhalothrin.Tukey)
PesticidesHSD=HSD.test(Cyhalothrin_aov, "Zones", group=TRUE)
print(PesticidesHSD)

#.....Anova Data analysis for Prawn.....
Lamda_cyhalothrin_prawn=c(0,0,0,0.563900494,1.898373212,2.628972022)
prawns_pesticides=data.frame(Zones=factor(Zones),Response=Lamda_cyhalothrin_prawn)
summary(prawns_pesticides)
prawns_pesticides_lm=lm(Lamda_cyhalothrin~Zones)
ANOVAprawn=anova(prawns_pesticides_lm)
print(ANOVAprawn)

#.....Testing means significance for Zones in Prawns.....

Cyhalothrin_prawns_aov=aov(Lamda_cyhalothrin_prawn~Zones)
Cyhalothrin.Tukey_prawns=TukeyHSD(Cyhalothrin_prawns_aov,"Zones")
print(Cyhalothrin.Tukey_prawns)
plot(Cyhalothrin.Tukey_prawns)
PrawnsHSD=HSD.test(Cyhalothrin_prawns_aov, "Zones", group=TRUE)
print(PrawnsHSD)
```

Appendix 6: Mean separation in heavy metals

```
$groups
      prawns$Hg_conc groups
Kisiju      0.18593667      a
Bagamoyo    0.07474111      a
Kilwa       0.05093167      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      prawns$Pb_conc groups
Kilwa      24.90741      a
Kisiju     24.75309      a
Bagamoyo   24.29012      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      prawns$Zn_conc groups
Kilwa     166.0582      a
Kisiju    153.8889      b
Bagamoyo  107.1627      c

attr(,"class")
[1] "group"
> |
```

```
$groups
      sediment$Cd_conc groups
Bagamoyo    1.796407      a
Kisiju      1.634232      ab
Kilwa       1.497006      b

attr(,"class")
[1] "group"
> |
```

```
$groups
      sediment$Hg_conc groups
Kisiju      0.049644      a
Bagamoyo    0.047935      a
Kilwa       0.035306      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      sediment$Pb_conc groups
kilwa      35.06944      a
Bagamoyo   31.66152      a
Kisiju     28.12500      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      sediment$Zn_conc groups
Kisiju     153.4888      a
Bagamoyo   152.4967      a
kilwa      133.4408      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      water$Cd_conc groups
Bagamoyo   0.14735165      a
kilwa      0.03758463      b
Kisiju     0.01767224      b

attr(,"class")
[1] "group"
> |
```

```
$groups
      water$Hg_conc groups
Bagamoyo   0.03011778      a
Kisiju     0.02873917      a
kilwa      0.02863750      a

attr(,"class")
[1] "group"
> |
```

```
$groups
      water$Pb_conc groups
Bagamoyo   1.20936214      a
kilwa      0.43518519      b
Kisiju     0.02237654      c
```

```
$groups
      water$Zn_conc groups
Bagamoyo   0.6392196      a
Kisiju     0.4928902      ab
kilwa      0.3862434      b
```